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Note: Detecting flow velocity with high purity semiconducting single-walled carbon nanotubes

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We report the measurement of fluid velocity on a semiconducting single-walled carbon nanotubes film in a microfluidic channel. To investigate the mechanism related to electrical signal change, we performed various experiments along with changing the flow velocity, the ion concentration and liquid viscosity, etc. Our result suggests that the sensing of flow velocity is a closely related to a pulsating asymmetrical thermal ratchet model. The electric signal change was strongly dependent on the electrode alignment, and the channel width of the sample. As the result, we achieved highly sensitive detection of the fluid, roughly 4 times greater than previous results. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4797620]

Carbon nanotubes (CNTs) have been studied because of their extraordinary mechanical[1] and electrical[2] properties and structural characteristics.[3] CNTs have shown great promise for the development of technological applications, such as nanoelectronics,[4] electrochemical actuators,[5] composite,[6] conductive electrode,[7] and sensors.[8] In particular, nanotube- and fluid-flow-based sensors and energy devices have gained increasing research interest.[9–14] It is appealing to integrate the nanoelectronics and microfluidic advantage of single-walled carbon nanotubes (SWCNTs) into one chip. This integration will enable electrical probing the extremely small rate of flow (less than 10 mm/s). Because the detection limits of commercial thermal flow sensors are 10 mm/s at most.[15] Recently Bourlon *et al.*[13] showed that electrolytically gated SWCNT transistors could sense the local potential generated by a fluidic flow of ionic solutions on charged surface. And Kim *et al.*[14] demonstrated flow velocity sensing of an electrolytic solution in a microfluidic channel using silicon nanowire (SiNW) field effect transistor (FET) sensors. Although many researches have been conducted, still it need to be enhanced the resolution of sensor to detect the extremely low range of velocity (0.01–10 mm/s) that commercial flow sensor could not detect. The limit of detection which can be detected by individual carbon nanotube FET sensor and p-type SiNW are 20.83 mm/s and 0.55 mm/s, respectively. Furthermore, sensors based on single-element nanomaterials may suffer from irregularity due to the different properties of different materials, and there are many obstacles to overcome for practical applications as flow sensors.

In this Note, we proposed a high-sensitivity flow sensor based on a high-purity s-SWCNT film in a microfluidic chip which can overcome the limitations of previous studies for the first time. We found that s-SWCNT which is more sensitive than that of m-SWNCT or mixed ones in previous study.[16] Based on these experiments results, we made the network type device with s-SWCNT for developing the flow sensor. We verified the main mechanism related to electrical signal change with several factors (flow velocity, concentration of ion, and liquid viscosity). And we investigate how to enhance the sensitivity of sensor with electrode alignment, channel width. Finally, we could detect the flow velocity (0.01 mm/s) and developed the flow sensor which is easy to fabricate and robust to flowing liquid.

The detailed fabrication process is depicted in Fig. 1(a). The electrodes were fabricated by standard technique of lift-off on glass wafers.[17] After fabrication of the electrodes, the wafer was cut into smaller substrates (22 mm × 18 mm) for transfer of the CNT film. We used previously separated s-SWCNTs which were purchased from NanoIntegris Inc. SWCNT films (5 mm × 5 mm) were prepared using a vacuum filtration method.[18] The resistance of the CNT film was ~2 kΩ. We transferred the SWCNT film onto the metal (Au) electrodes pre-deposited on a glass substrate. To avoid loss of the SWCNTs on the glass during fluid flow, we applied a 50-nm-thick UV resin (less than the thickness of the SWCNT film) using a spin coater at 3000 rpm for 30 s, followed by annealing under a UV lamp for 120 s under vacuum. Finally, the complex device was covered by a polydimethysiloxane (PDMS) block, in which a 0.1-mm-high, 1.5-mm-wide, and 20-mm-long fluidic channel was defined by replication molding.

We prepared two kinds of samples with the electrode aligned parallel to flow (type-1) and perpendicular to the flow (type-2) in Fig. 1(b). A syringe was filled with various solutions (H_2O, KCl, D_2O) and attached to the inlet using a capillary in Fig. 1(c). The syringe, driven by a syringe pump, injected the fluid into the fluidic channel at a well-controlled rate so that the fluid flowed directly onto SWCNT device. The electric signal changes in the CNT sample were measured using a digital multimeter (DM2002, Keithley Instruments) connected to a data acquisition system. All experiments were carried out at room temperature.

It is well known that the electric signal changes when CNTs are immersed in flowing liquids. We consider three

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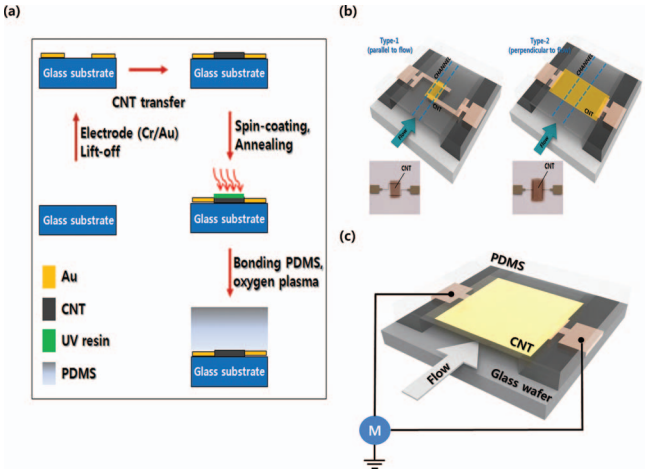

FIG. 1. Experimental setup. (a) Fabrication process of the sample. (b) Two kind of samples. (c) Schematic view of experimental setup.

previously proposed mechanisms. The first mechanism based on momentum transfer from flowing liquid molecules into acoustic phonons in nanotubes. The free carrier charges can be dragged by the flow.[9] The second mechanism is a pulsating asymmetric thermal ratchet model for current generation due to fluctuating Coulombic potentials and phonon dragging by Gosh *et al.*[10] The third mechanism is the streaming potential in nanomaterials, which has been investigated previously.[11,12] To verify these theories, we investigated the electric signal change induced by liquid flow over s-SWCNTs with various flow velocities, ionic strength and liquid viscosity.

Figure 2(a) shows a typical voltage response as a function of time when DI water flow was switched on and off according to the flow direction (forward and backward). Compared to stagnant liquid, the voltage change was distinct and exhibited an equivalent pattern. When we injected the

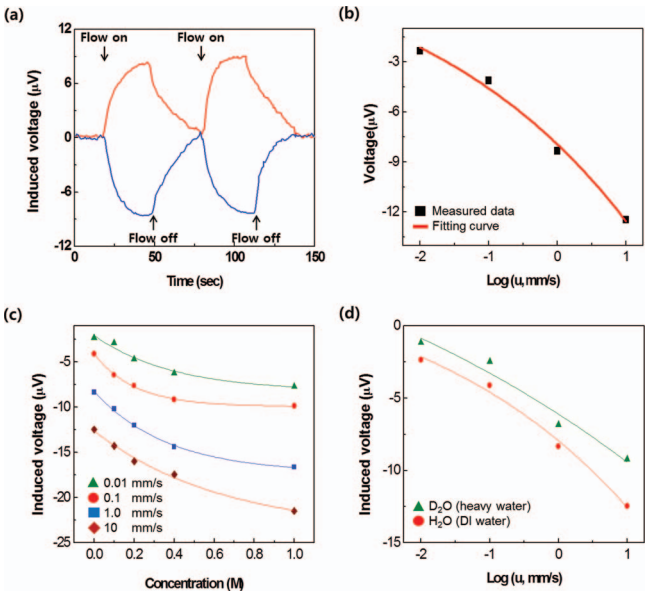

FIG. 2. Change in the electrical signal (voltage) of s-SWCNTs. (a) The open-circuit voltage at a flow velocity of 1 mm/s (forward: blue line, backward: red line). (b) Dependency of the voltage and flow velocity. (c) With various concentrations of KCl. (d) With heavy water (D_2O).

deionized (DI) water on the s-SWCNTs sample, the peak direction was opposite that of the metallic SWCNTs or mixed CNTs. This was likely due to the s-SWCNTs p-type characteristics, with holes as the primary charge carrier, whereas metallic SWCNTs have electrons charge carriers. Thus, as the ions in solution fluctuated near the nanotube surface, their detected voltages appeared as a reversed signal, similar to previous research.[16] When the flow was turned on at a velocity of 1 mm/s, the voltage signal (blue line) changed from zero to -8.33 μV. When the flow was turned off, the voltage gradually returning to zero within 30 s. The alternating on-off water flow produced a series of trapezoid-wave-like voltage signals.[16] The voltage (red line) is measurement for flow velocity of 1 mm/s in the opposite direction in Fig. 2(a). These results can be explained by a mechanism in which voltage generation is closely related to phonon drag due to flow, as proposed previously.[9,10]

We also measured the voltage change as the flow velocity increased (0.01, 0.1, 1, and 10 mm/s). Figure 2(b) shows the dependency of the electric signal changes on the flow velocity for DI water. The voltage dependence (red line) can be expressed by nonlinear exponential fitting curve. Although the fitting parameters were varied according to the experimental factors, the patterns of fitting line were almost similar. The absolute value of slope at log scale of x axis definitely increased at high flow velocity (u, mm/s).

Figure 2(c) also shows a plot of the electric signal change with concentration using KCl as the electrolyte. The ionic strength of the KCl solution was varied (0.1, 0.2, 0.4, and 1.0 M). The electric signal change was proportionally dependent on the ionic strength. A voltage of -21.47 μV was detected at a flow velocity of 10 mm/s. The voltage in KCl (1.0 M) was roughly two times greater than the voltage (-12.46 μV) detected in the DI water at the same flow velocity. And to investigate the effect of viscosity (η) on voltage signal change, we carried out experiments using D_2O (heavy water). The heavy water ($\eta = 1.25$ mPa s) has much higher viscosities than DI water ($\eta = 0.9$ mPa s). We observed that the electric signal change fell with increasing fluid viscosity in Fig. 2(d). When we increased the viscosity from 0.9 mPa s (DI water) to 1.25 mPa s (heavy water) at a velocity of 10 mm/s, the electric signal change decreased about 26% from -12.46 μV to -9.21 μV.

We conducted various experiments for verification of mechanism. Based on these experiment results, it appears that pulsating asymmetric thermal ratchet model is the main mechanism responsible for voltage change in our experiments. Because our experiment results are matched up with theory of previous study (logarithmic dependence of velocity and voltage, strong dependence of ionic strength of fluid).[10] Streaming potential model, requiring ionic species in solution, is unlikely since no salt was added, and the pH was approximately 5–7, meaning that approximately only 1 in 10^7–10^9 water molecules was a hydronium or hydroxide ion.

As mentioned above, we could detect the flow velocity as low as 0.01 mm/s. This result is much lower than the previously reported measured velocity of, 0.55–1.1 mm/s using a SiNW, and 20.83 mm/s using an individual CNT.[13,14] To enhance the performance of sensor, we conducted experiments

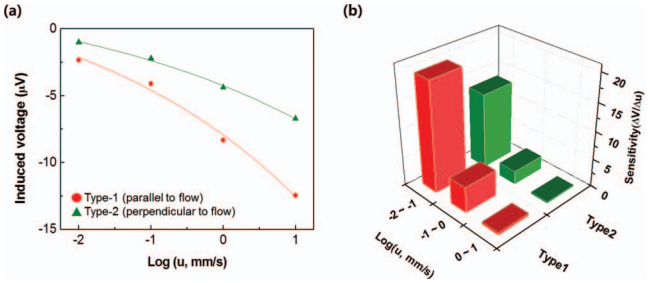

FIG. 3. Effect of electrode alignment. (a) The electric signal change. (b) The sensitivity of the sensor. (Type-1: parallel to flow, Type-2: perpendicular to flow.)

with electrode alignment, channel width. First we investigated the effect of electrode alignment on the sensitivity of sensor. We changed the flow velocity of the DI water (0.01–10 mm/s) for each sample in Fig. 3(a). We compared samples under the same conditions: the detected voltage ($-1.02\,\mu$V) for the type-2 was half that ($-2.34\ \mu$V) for type-1 at 0.01 mm/s. When we increased the flow velocity to 1 mm/s, the electric signal change were $-4.38\ \mu$V and $-8.33\ \mu$V, respectively. And the sensitivity was calculated by dividing the voltage change at a specific velocity by the change of the flow velocity,

$$\eta = \Delta V_{oc}/\Delta u. \tag{1}$$

Prior to discuss the sensitivity of sensor, we have to limit the scope of flow velocity. As described in Fig. 3(b), the sensitivity was decreased as the flow velocity increased. So we analyzed the sensitivity of sensor in relatively low velocity range (0.01–0.1 mm/s). The sensitivity of the s-SWCNTs was dependent on the electrode alignment. For example, at a flow velocity range of 0.01–0.1 mm/s with DI water, the sensitivity of type-1 was 1.46 times higher than that of type-2.

We further investigate the effect of channel width. As we increased the channel width from 0.5 mm to 3.0 mm, the electric signal change was increased in Fig. 4(a).

When we used a 3.0-mm-width of channel at a fixed velocity of 0.01 mm/s, the detected voltage was $-4.21\ \mu$V, 5.7-fold increase compared to the 0.5-mm-width (-0.74μV). The more CNTs expose to the electrolytic solutions, the more interactions between the water molecules and free charge carriers in the s-SWCNTs increased. The sensitivity also increased with increasing channel width in Fig. 4(b). For example, at a flow velocity range of 0.01–0.1 mm/s, the sensitivity of 3.0 mm was 3.5 times higher that of 0.5 mm.

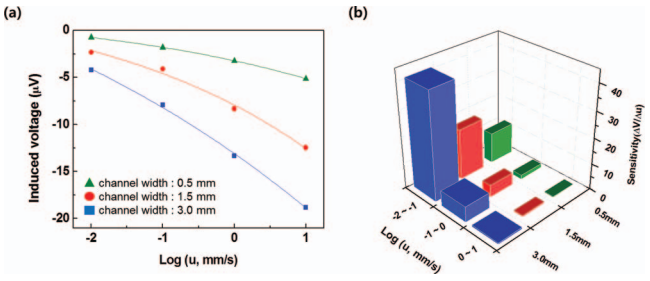

FIG. 4. Effect of channel width. (a) The electric signal change. (b) The sensitivity of the sensor.

Moreover, we investigated how to enhance the performance of sensor and found that electrode alignment and channel width are strongly dependent on the performance of the sensor in extremely low velocity range (0.01–0.1 mm/s). At fixed flow velocity of 0.01 mm/s with DI water, the flow-induced voltage ($-4.21\ \mu$V) from s-SWCNT film (parallel type and 3-mm channel width) is roughly 4 times greater than the voltage ($-1.02\,\mu$V) from s-SWCNT film (perpendicular type and 1.5-mm channel width).

In summary, we demonstrated that a flow sensor based on s-SWCNTs produced an electrical signal change in response to fluid flow and could be used to detect extremely slow flow velocity down to 0.01 mm/s. We concluded that main mechanism responsible for electric signal change is pulsating asymmetric thermal ratchet model rather than streaming potential model. Additionally, we investigated the optimal conditions for enhancing the performance of sensor. The flow sensor has the potential to sense a wide range of flow velocities, the flow direction, and ionic strength at a given flow velocity.

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