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Network Single-Walled Carbon Nanotube-Field Effect Transistors (SWNT-FETs) with Increased Schottky Contact Area for Highly Sensitive Biosensor Applications

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Since the first demonstration of an electrical nanobiosensor using a silicon nanowire-field effect transistor (SiNW-FET) device,[1] there have been many attempts to exploit label-free electrical sensing systems using similar types of nanomaterials.[2−4] Single-walled carbon nanotubes (SWNTs) are one of the promising candidates due to their high biocompatibilities[5] and well-established knowledge about their device properties.

One uprising issue of such a system is sensitivity. Recently, array-type devices made of n- and p-doped SiNWs combined with microfluidic channels have been demonstrated as a multiplex biosensor system with approximate femtomoles of protein detection limits.[6] In the case of a SWNT-FET device, however, the reliable detection limit for the sensing of proteins or protein−protein interactions is ca. 100 pM to 100 nM.[4a,b] The relatively lower sensitivity of the SWNT device is intimately related to the sensing mechanism and the corresponding device geometries. In contrast to SiNW devices, which sense protein interactions via the chemical gating effect, SWNT devices are operated by the Schottky barrier (SB) modulation effect[4b,7] as well as by the chemical gating effect.[3a,4e,f] The SB effect will dominate especially when the isoelectric point (pI) of a protein is close to the pH of the reaction media.[4b]

Herein, we report substantially improved sensitivity of SWNT-FET devices by modifying the geometry of the devices as they have increased Schottky contact area. This has been achieved by evaporating metals for source and drain electrodes using a shadow mask at a tilted angle during the device fabrication (Figure 1).

For the fabrication of such devices, network SWNTs (av. diameter = 1.7 nm) were synthesized on SiO_2/Si wafers by chemical vapor deposition (CVD) method as previously reported (Figure 1c).[5b,8] Thin aluminum shadow masks with a width of 200−300 μm were suspended on the SWNT area[9] and then were transferred into a thermal evaporator equipped with 23° tilted sample stages (Figure 1a). During the evaporation of Cr (15 nm) followed by Au (30 nm), metals were guided to penetrate underneath the shadow mask. Such devices show very little gate field dependence, that is, pseudo-metallic transport characteristics (Figure 2a,b). This abnormal transport property seems to be due to suppressed field efficiency shielded by percolated metals covering the surfaces of SWNT channels, which is also indicative of the formation of thin and wide Schottky contact area (Figure S1 in Supporting Information).

The devices with increased Schottky contact area have shown high sensitivity with 1 pM detection limit for nonspecific bindings of proteins as well as specific bindings of protein pairs. This is a 10^4-fold increased detection limit compared to that of the reported similar nanotube-based devices, especially for specific protein−protein interactions. First, we tested the sensitivity of devices for nonspecific bindings of various proteins. All of the experiments were performed in a homemade Teflon electrochemical cell (Figure S2 in Supporting Information), which is designed to expose both Schottky contact area and SWNT channels to protein solutions.

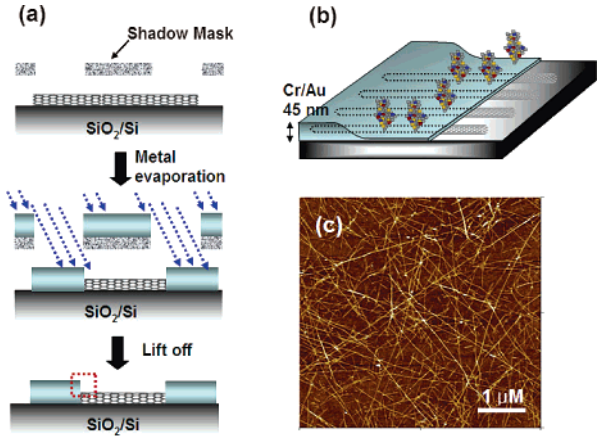

Figure 1. (a) A schematic view of the fabrication of a network SWNT-FET device using a shadow mask at a 23° tilted sample stage. (b) A detail view of the dashed square area in (a), which depicts the formation of a thin and wide Schottky contact area. (c) An AFM image of CVD-grown network SWNTs used for device fabrications.

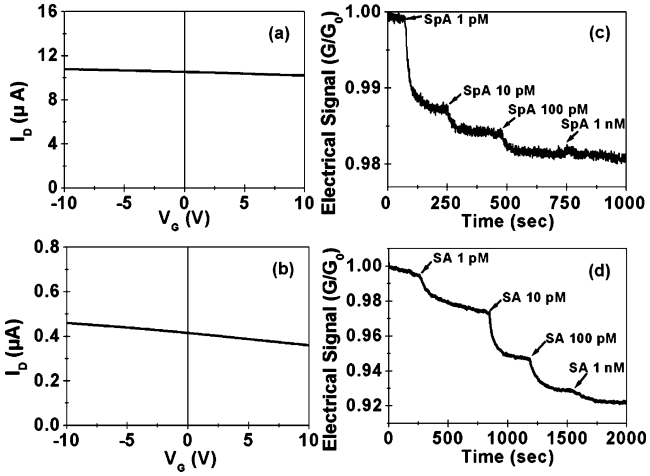

Figure 2. Electrical sensing of nonspecific bindings of (c) SpA and (d) SA using network SWNT-FET devices of which $I-V_g$ curves represent pseudo-metallic characteristics (a, b); V_{ds} = 10 mV.

The devices were installed into the electrochemical cell, then filled with phosphate-buffered saline (PBS, 10 mM, pH = 7.4) solution while 10 mV of bias voltage (V_{ds}) was continuously applied between source and drain electrodes. When the devices started to show a steady current, proteins at specific concentrations were injected into the cell using a micropipet. To compare the sensitivity of our devices with that of the ones fabricated by photolithography,[4b]

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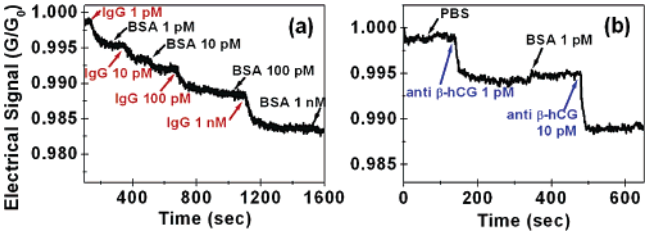

Figure 3. Electrical sensing of specific protein pairs of (a) SpA (probe)−IgG (target) and (b) hCG (probe)−anti β-hCG (target) using network SWNT-FET devices (V_{ds} = 10 mV) (refer to $I-V_g$ curves, Figure S3 in Supporting Information).

we examined the same proteins used in previous reports, such as Protein A (SpA, derived from *Staphylococcus aureus*, Zymed), Streptavidin (SA, Sigma), mouse antibody β-hCG (anti β-hCG, Lab Vision), human chorionic gonadotropin (hCG, Sigma), and rabbit immunoglobulin G (IgG, Sigma).

All of the examined devices have shown significant conductance drops (>1% conductance change) upon nonspecific adsorption of proteins at as low as 1 pM concentration. Graphs c and d of Figure 2 show conductance drops upon the additions of SpA and SA, respectively, at various concentrations. Although slightly different extents of conductance drop have been observed from devices to devices, 12 out of 15 devices have shown 1 pM sensitivities with greater than 1% conductance drop. The rest of the three devices have also shown conductance drops at 1 pM of protein solutions but with high noise level and <1% conductance change.

The current devices have also shown 1 pM sensitivity level for specific bindings of protein pairs. Probe proteins were immobilized on the devices by immersing as-fabricated devices into the concentrated probe protein solutions for 3 h followed by the treatment with Tween20 (0.05 wt % in PBS solution) for 2 h. The Tween20 treatment protects unoccupied sites of the device from nonspecific bindings (Figure S2 in Supporting Information). Once the devices are stabilized, target proteins of various concentrations were injected stepwise. Graphs a and b of Figure 3 show systematic conductance drops upon the specific recognitions of SpA by IgG and hCG by anti β-hCG, respectively. The devices show apparent conductance drops at 1 pM of target proteins. From the fact that control injections of PBS and bovine serum albumin (BSA) have not changed the conductance, it is confirmed that the conductance drops are solely attributed to the specific bindings between probe and target proteins.

The substantially increased sensitivity is primarily due to the thin and wide Schottky contact area on which relatively more numbers of proteins can adsorb at low concentration, resulting in prompt modulation of metal work function of the devices. The formation of thin and wide metal coating by shadow mask angle-evaporation has been confirmed by AFM, which clearly shows the evaporated metals having a gradient thickness over a wide range of area (Figure S4 in Supporting Information). Control experiments tested with devices containing identical CVD-grown SWNTs, but fabricated without angle-evaporation, generally respond to protein adsorptions at >10 nM (Figure S5 in Supporting Information). Moreover, it is also critical for protein to be adsorbed on a thin metal Schottky contact area since there has been no response when a micro-droplet of PBS and proteins is placed on thick metal surfaces which are 45 nm vertically away from the Schottky contact interface, even at very high protein concentration (>micromole) (Figure S6 in Supporting Information).

Along with the increased Schottky contact area, internanotube Schottky contacts may further increase the sensitivity. Since the network SWNTs grown in high yield by CVD naturally populate both semiconducting and metallic nanotubes, the Schottky point contacts are formed in high population where semiconducting and metallic SWNTs are crossed.[10] More details about the effect of internanotube Schottky contact are still under investigation.

In summary, we have fabricated highly sensitive network SWNT-FET devices, which have successfully detected both nonspecific adsorptions of proteins and specific protein−protein interactions at 1 pM concentrations. The increased sensitivity is mainly accredited to the increased thin and wide Schottky contact area, which has been achieved by evaporating electrode metals using a shadow mask on a tilted angle sample stage. The accomplishment of highly sensitive SWNT devices is expected to accelerate the progress toward the realization of nanoscale and label-free electronic biosensor systems.

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Supporting Information Available: Control experiments, AFM images of devices, and more information. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) A 15 μm thick Al foil was manually cut into a strip (200 μm × 1 cm) then placed onto a SWNT network containing SiO_2/Si substrate of which the edges were blocked by double-sided tape. The strip gently placed on the double-sided tape architects ca. 50 μm gap between the substrate and the mask.
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