4. Results and Discussion

4-1 Selecting operative CNT devices

At first, we want to know whether the CNT successfully cross-links the sensing window between the source and the drain. Therefore, we characterized the basic I-V curve of the CNT FET device. The measured drain current (I_D) versus drain voltage (V_D) was obtained in the ambient air by semiconductor parameter analyzer HP 4156 (Fig. 13). The result indicated that CNT had successfully bridged over two metal electrodes. The Schottky barrier height which exists in the metal-semiconductor junction (Rhoderick et al., 1970) is the rectifying barrier for electrical conduction across the metal-semiconductor junction and, therefore, is of vital importance to the successful operation of any semiconductor device. When electrons transfer from the metal into the semiconductor, they need to overcome the energy barrier. Therefore, we have to offer a supplementary energy for this requirement. When the supplementary energy is lower than the energy barrier, the I-V curve presents a horizontal pattern resulting from electrons can not overwhelm the energy barrier. When the energy of electrons is higher than the energy barrier, electrons cross the energy barrier and the I-V curve ascends with the increased voltages. The resulted curve demonstrated that the CNT successfully cross-linked the sensing window between two metal electrodes.

While measuring each one of the devices, we found different features among them. These were resulted from the differences of metal and semiconductor conduction properties of CNT, of the undefined length of CNT between two pads, of the unclear amount of CNT between two pads, and of the conductivity of the metal-semiconductor junction between different devices. Accordingly, we wanted to know whether the conductivity of the devise itself was affected by ambient air and liquid solutions.

We pick an operative CNT device to detect the variation of different solutions. The CNT device was further confirmed by an atomic force microscopy (AFM), which clearly presents the image of CNT in the sensor window (Fig. 14). The AFM also demonstrated the diameter of the CNT was 1.4nm and the length between two pads was 2 um.

At the same time, we exhibited that the side-by-side layout of CNT device displayed high ratio of operative devices. In the study, we designed two types of devices patterned by end-to-end and side-by-side (Fig. 15). The results showed that the layout of side-by-side had 86% of the operative rate and the end-to-end layout only had 3.2%. This demonstrated that the side-by-side layout contained an efficient performance because the length between two pads (～62μm) in this pattern are longer for more CNT to deposit. Therefore, we chose the side-by-side layout as the detector in our experiment.

4-2 I-V curves of CNT by two-terminal methods in solutions and distilled water

We measured electrical transductions of the fabricated CNT FET device by two-terminal method at room temperature. No variety of I_D -V_D curve was seen by dropping distilled water (resistivity～18.2 MΩ－cm) and NaCl solution (1x10^{-6}M-1M) into the sensing window of the CNT device(Fig. 16). Result was not anticipated that drain currents were higher in NaCl solution than those in the distilled water because of higher ionic concentrations. Before continuing the following manipulation, we should understand the mechanism of FET sensor. Some possibilities were that charges on bio-molecule surfaces performed gating effects or charge transfer to nanotubes so that they induced electrical conductances of the nanotube FETs (Chen et al., 2003; Chen et al., 2004; Cui et al., 2001; Star et al., 2003). Another suggestion was that one bio-molecule adsorbing on the devices affects the value of dielectric constant of the electrical double layer in aqueous solution by which these changed the gate efficiency of the electrolytes (Bard et al., 1980). Because distilled water and NaCl solutions were neutral, positive and negative charges could evenly distribute in these solutions. Accordingly, the CNT surface was enclosed with the neutral solution. This designation did not change the value of dielectric constant of the electrical double layer and no variation of I_D -V_D curve was determined by two-terminal measurement in this study. On the other hand, I_D -V_D curve between solution (distilled water and NaCl solution) and ambient air showed slight different while the voltage was higher than 0.5V. This resulted from that the oxygen of water molecules donated their electrons to the surfaces of CNT so as to change the conductance. Furthermore, the passivated CNT devices could discriminate different conductivities of nanotubes between ambient air and solutions.

4-3 I-V curves of CNT by three-terminal methods in solutions and distilled water

In order to separate negative and positive charges in the drop on the devise, we apply a gate into the drop. The gate differently induced changes between bake-gate and liquid-gate (Krüger et al., 2001). The insulator layer was usually thick. The liquid-gate was 200 times more effective than that of the back gate. Here, the liquid-gate was applied to establish an electronic potential in the solution related to the device (Krüger et al., 2001; Rosenblatt et al., 2002). When a positive voltage was applied to the liquid-gate, the CNT-electrolyte interface was polarized by the attraction of cations. The result was reverse while a negative gate voltage was applied to the liquid-gate. So, the I-Vsd characteristics were measured by adding different liquid-gate voltages ranging from -1.5V to 1.5V in steps of 0.3V.

Various currents were obtained by estimating drain currents of the device in distilled water cooperating with various voltages of liquid-gate (Fig. 17). The data indicated that the device in solutions shared same properties of conventional FET. Drain currents increased with elevated voltages of the liquid gate. The result was important as semiconductor material usually avoided contacting with water. When it contacted to water, shorting out happened. The result demonstrated that the passivated device worked as conventional FET in distilled water. Similar was also obtained in the NaCl solution (Fig 18). However, bio-reactions usually take place in the aqueous environment. The result suggested that the passivated devices might be applied to bio-sensor in the future.

4-4 Discriminating p- or n-type of passivated CNT devices

Obtaining both p- and n-type materials and controlling their charge carrier densities were crucial to the current microelectronics. With CNT, an interesting phenomenon is that tube-FETs under ambient conditions are always p-type with holes as the majority carriers (Shim et al., 2001). Here we used liquid-gate to discriminate the types of the passivated CNT device in aqueous solution. We provided various voltages on liquid-gate from -1.5V to 1.5V. An apparent variation was observed in positive voltage increased from 0 to 1.5V (Fig. 19). It illustrated that positive voltage of liquid-gate induced the change of the carrier density of the CNT. Further, there was no change between negative voltages ranging from 0V to -1.5V. It indicated that the negative voltage of liquid-gate difficultly altered the density of carriers of the CNT. Figure 20 shows that the turn-on voltage of positive voltage happened at the voltage from 0.75 to 1V. Positive voltage turned on the passivated CNT device in lower voltage. However, the turn-on voltage of negative voltage happened at the voltages around -1.5V. It presented that the negative voltage need higher voltage than -1V to turn on the device. It revealed that positive voltage of liquid-gate was easier to alter the carrier density than that of negative voltage. Thus, we considered that it was an n-type CNT FET which current rose following the increased positive voltage of liquid-gate. The dominance of one carrier in a semiconductor might be the result of doping, a bulk effect, or it may be determined by Schottky barriers at the metal-semiconductor junction (Derycke et al., 2002). These barriers allowed the injection of only one type of carriers including electrons or holes and were sensitive to the electrostatic effects. Charge transferred by foreign species adsorbed at the junctions. The evident electrical behavior was dominated by its effect on the contact barriers. In air or oxygen, the Fermi level was extrinsically pinned near the valence band maximum, and this pinning was responsible for the p-character of air-exposed

CNTFETs. The outgassing of the device changed the band-bending near the contacts, and the position of the Fermi level within the band-gap changed as a function of the amount of oxygen present at the contacts. This model was illustrated in Fig. 21, which gives a qualitative picture of the bending of the bands of a p-type and an ambipolar CNTFET near the contacts. So, negative charges were the major member in the CNT. When we provided positive charges, which induced the accumulation of negative charges, the ID -VD curve variation became more obvious. The passivated CNT FET presented as an n-type characteristic of FET. It also demonstrated that the passivated CNT FET constitutively presented as an n-type characteristic of FET in aqueous solution.

4-5 Comparing leakage currents of the devises passivated or non-passivated layers

A photoepoxy was firstly used to form protection layers, cover entirely source/drain electrodes (Someya et al., 2002). Another study also indicated that the preparation of these protection layers was crucial to useful measurement of conductance of semiconducting nanotubes under the aqueous environment (Someya et al., 2003). For example, where the droplet size exceeded several hundreds micro meter, water-mediated leakage current between source/drain electrodes and/or water-associated gate-leakage currents were dominant and measurement of conductance of nanotubes became impossible. When water droplets of several tens of microns in diameter were delivered onto unprotected devices, it avoided leakage mentioned earlier, but electron transport in the nanotube was quenched (Someya et al., 2003). So, preparation of the protection layer was crucial for measuring conductance of semiconducting nanotubes in water environment. Here, the passivation layer was designed to decrease the leakage current. We studied the relationship via measuring current I_D, I_S, and leakage current. The measured current of I_S and I_D with leakage current of Ig was presented in Fig. 22. It obviously indicated the curves of $|I_D| = |I_S|$ which were higher than that of Ig. The measured current was higher than the value of $1x10^{-10}$A and the leakage current was lower than the value of $1x10^{-11}$A. We compared the leakage currents of with- and without- passivated devises in distilled water and the result was presented in Fig. 23. Result indicated that the non-passivation device has leakage current around $1x10^{-6}$ to $1x10^{-8}$A. The passivated devise has lower leakage current of $1x10^{-11}$A. Results demonstrated that the passivation layer apparently decrease the leakage currents about 2-3 exponential orders. Low leakage currents of the CNT devices were important for biological applications. Because low leakage current did not cover the low measuring currents, the result enhanced the operative range of the device at fixed V_D range. For example, as shown in Fig. 24, the dash line represented the leakage current of non-passivated device. When the leakage current presented in the range of the dash line, the strong leakage current covered most of the measured currents. The covered currents included all of the linear ranges. When the leakage current was low, we selected a higher value of V_D. In Fig. 22, we initiated with drain voltage of 0.0V or 0.1V. However, when leakage current was higher than most of the measured currents, we chose only a narrow range of I-V, which originated from 0.4V or 0.5V. The effective range of the VI was narrow and we could not identify a more effective measuring current of the linear range. The higher leakage current restricted the development of high sensitive sensor in the future. The photoresistor layer also kept the leakage current at the low voltage (1×10^{-11}A) which did not switch to a higher value following the increased liquid-gate voltage. Here, we also measured the leakage current of the non-passivated CNT devices in NaCl solution. The result was similar to that in deionized water (Fig 24). It demonstrated that the passivated CNT FET still kept at low leakage current in ion solution. It suggested that the passivated CNT FET has the potential to be developed for the application in bio-sensors.

4-6 Studying the conductivities of the devices in distilled water and NaCl solution

We utilized the passivated CNT device to distinguish the difference between distilled water and NaCl solution by adding a liquid-gate electrode (Fig 25). In the study, the distilled water curve and the NaCl solution curve overlapped at 0.3V. The result indicated that when the liquid-gate voltage was as low as 0.3V, the curve of distilled water and NaCl solution could not be distinguished. When the liquid-gate was as high as 0.9V or 1.5V, the measured currents were revealed that the I-V curve of the NaCl solution was higher than that of the distilled water. The result indicated that when the voltage of liquid-gate was higher than 0.9V, distilled water and NaCl solution could be distinguished by the passivated CNT device. This resulted from that the high voltage of liquid-gate distinguished the differences between distilled and NaCl solution. When the voltage was higher than a particular range, the charge was separated in the solution. The ion concentration near the surface of the CNT between the distilled water and the NaCl solution was different and the dielectric constant of the electrical double layer between them also differed. So, the passivated CNT device was utilized to distinguish between them by a high voltage of liquid-gate.

4-7 Investigating the conductivities of the devices in solutions of various NaCl concentrations

Some bio-reactions change the ion concentration in the environment. Here, we distinguished the different of ion concentration of NaCl solution by the passivated CNT device (Fig 26). The I_D-V_D curves of different concentrations of NaCl solution, ranging from $1x10^{-6}$M to 1M, were separated under constant voltage of liquid-gate.

The results demonstrated that the CNT device was capable of determining the ion concentrations in aqueous solution by a liquid-gate to induce the separation of charges. Therefore, the passivated CNT devices at certain biasing conditions were environmentally sensitive. It also implied that the CNT device was practically employed to detect the ions produced by specific biological reactions. Here, we probed into the detail of the Fig. 26. The mechanism for the transfer of electrons in the CNT was very complicate. Less concern would affect the complicate mechanism of the little drop of the solution. The passivated CNT device could distinguish the difference of the ion concentration (Fig 26). However, it was not regular changes from $1x10^{-6}$M to 1M. Here, we chose a same property of the different concentration curves and compared the relation between them. First, we divided them into two groups. $1x10^{-6}$M and $1x10^{-4}$M were for mechanism 1 and $1x10^{-2}$M and 1M were for mechanism 2. The fashion of the curve of the same group was conserved. Further, we speculated that the NaCl solution would cause the reversion of the CNT from n-type to p-type. We supposed that Na^+ or Cl^- doped the CNT and to tuned the charge carrier densities of the CNT. We saw that the I_D-V_D curve of $1x10^{-6}$M was higher than that of $1x10^{-4}$M (Fig 26). The result indicated that the current measured in $1x10^{-6}$M is higher than that in $1x10^{-4}$M. It presented that lower concentrations induced higher measuring currents, and it also illustrated that the CNT reversed from n-type to p-type. The result was identical to mechanism 2. The I_D-V_D curve of $1x10^{-2}M$ was higher than that of 1M and the lower concentration made higher curve of measuring current. We elucidated the above outcome by simple methods and other details will be discussed in the future.