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Semiconducting single-walled carbon nanotube networks-based double-gate thin-film transistors for high performance aqueous chemical sensor applications

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Abstract

In this paper, we have fabricated a highly sensitive separative extended gate chemically modified field effect transistor (SEG-ChemFET) sensor using semiconducting single walled carbon nanotube (scSWCNT) network. To improve the stability and sensitivity of the scSWNT channel layer, we fabricated a double-gate structure FET transducer with passivated channel by top- and bottom-gate insulators and applied a separated sensing membrane. The scSWCNT network channel was formed by solution process. In order to increase the sensitivity, a low-k spin-on-glass (SOG) film and a stacked Ta_2O_5/SiO_2 film are formed as top-gate and engineered bottom-gate insulators, respectively, improving the coupling ratio. As a result, the fabricated scSWCNT ChemFET sensor has a 365.65 mV/pH sensitivity which is much higher than the Nernst limit (59.5 mV/pH), a linearity of 99.88%, and a drift rate of 72.44 mV/h, and thus high sensitivity biosensor applications are expected.

1. Introduction

Semiconducting single-walled carbon nanotubes (scSWCNTs) have been studied extensively as channel layers of thin-film-transistors (TFTs) due to their excellent electrical and mechanical properties. Compared with poly-Si, amorphous Si, or oxide semiconductors, which are widely used as TFT channels, they have advantages in transparency, flexibility, high mobility and solution processability at room temperature. Since these properties enable CNT biosensors to effectively detect living biological molecules [1], a variety of biosensors for detecting proteins, enzymes, and DNA using CNT TFTs have been studied [2,3]. However, the CNT channel surface reacts easily with oxygen or water molecules, causing instability of the threshold voltage, which is a serious problem for stable sensor applications. Such a stability problem can be suppressd by the passivation of the channel layer, but the formation of the passivation layer using CVD or ALD is disadvantageous in terms of manufacturing cost because it requires vacuum equipment and a long processing time. On the other hand, the solution process does not require vacuum equipment, is capable of large-area processing, has high productivity and cost effectiveness. Meanwhile, FET-based ion sensing sensors (ISFETs) have the advantages of real-time, label-free, reagentless, sensitive and selective detection of biological analysis in solution. Nevertheless, the sensitivity limit of conventional ISFETs is only about 59.5 mV/pH (Nernst sensitivity) [4]. Because biological materials such as DNA and proteins have small signals, low sensitivity is a challenge that must be overcome for biosensor applications. A double-gate FET sensor is an effective option to overcome the Nernst limit due to capacitive coupling between top-gate and bottom-gate.

In this experiment, we fabricated scSWCNT FETs with double-gate structure and achieved larger capacitive coupling and lower leakage current by applying an engineered bottom-gate insulator with a stacked structure of Ta_2O_5 and SiO_2 layers. In addition, a solution-based SOG low-k film was used as a top-gate oxide (also as a passivation layer) to improve the stability of the scSWCNT channel and to increase the coupling between the gates.

2. General Instructions

After standard RCA cleaning of the heavily doped n-type Si wafer, 20-nm-thick SiO_2 and 60-nm-thick Ta_2O_5 films were deposited to form an engineered bottom gate oxide. A uniform scSWCNT random networks layer was deposited using a scSWCNT solution (diameter range of 1.2-1.7 nm, length range of 300 nm), and the active region of the TFT was formed by photolithography and O_2 plasma ashing. A source/drain (S/D) electrode was formed by a 100-nm-thick Ti evaporation with an E-beam evaporator and a lift-off method, and then a 300-nm thick top gate insulator was formed by coating the SOG. 150-nm-thick Ti was deposited by an E-beam evaporator and a top gate electrode was formed by lift-off. Finally, S/D contact holes were formed by RIE to complete a scSWCNT FET device with a double-gate structure. Fig. 1 shows a scSWCNT FET with a double gate structure with a engineered gate oxide.

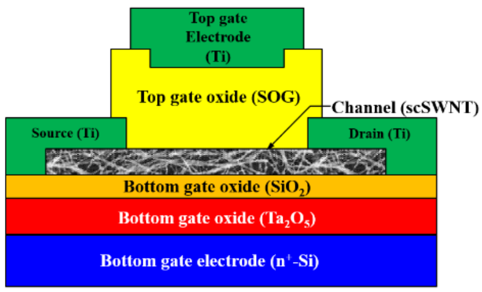

Fig. 1 Schematic structure of fabricated double-gate scSWCNT-TFT with engineered gate oxide.

In order to identify the sensitivity of sensing by capacitor coupling, we prepared two types of double-gate structure CNT TFTs with an engineered Ta_2O_5/SiO_2 gate oxide

(Device A) and a conventional SiO_2 gate oxide (Device B). Separative extended gate (SEG) was fabricated by sequentially depositing a 150-nm-thick indium tin oxide (ITO) film and a 50-nm-thick SnO_2 sensing membrane on a glass substrate, and then attaching PDMS (polydimethylsiloxane) reservoir. All electrical characteristics were measured using an Agilent 4156B Precision Semiconductor Parameter Analyzer equiptment in a dark box to avoid light and noise.

In the fabricated double-gate structure, capacitive coupling occurred by series capacitor composed of top-gate oxide/channel/bottom-gate oxide. In this configuration, the top and bottom surface potentials of the channel layer are affected by the opposite surface potential.

Particularly, in a fully depleted channel, the relationship of the threshold voltage according to the capacitance of each part is as follows [4,5]:

$$\Delta V_{th}^{T} = \frac{C_{CNT} \cdot C_{BG}}{C_{TG}(C_{CNT}+C_{BG})} \Delta V_{th}^{B} \qquad (1)$$

where ΔV^{T}_{th} is the threshold voltage shift of the top-gate sweep, ΔV^{B}_{th} is threshold voltage shift of bottom-gate sweep. C_{TG}, C_{BG} and C_{CNT} are top-gate oxide, bottom-gate oxide and the scSWCNT channel capacitances per unit area respectively. The equivalent oxide thckness (EOT) of the top-gate oxide of the fabricated device A and B is 375 nm, but the EOT of the bottom-gate oxide is 35 and 80 nm, respectively. Therefore, a high threshold voltage shift can be obtained by different capacitances at the top and bottom of the channel.

Fig. 2 shows the shift of the I_D-V_G curves of (a) Device A and (b) Device B in various pH buffer solutions of double-gate structure scSWCNT TFTs. The pH measurement of the buffer solution was performed by connecting the reference electrode and SEG to the bottom gate and sweeping the top gate voltage. As a result, the sensitivity and linearity of the device A and the device B were 365.65, 171.11 mV/pH and 99.88, 98.64%, respectively. Therefore, it was confirmed that the proposed double-gate structure scSWCNT TTF with engineered gate oxide can amplify the sensitivity much higher than the Nernst limit.

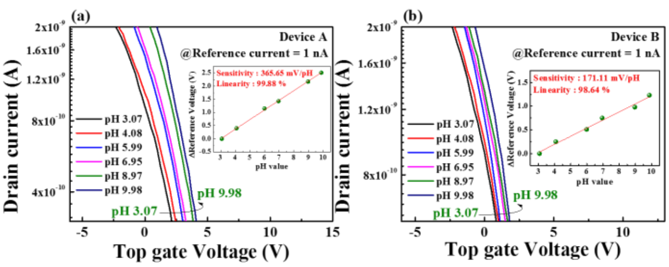

Fig. 2 Transfer characteristic curves of the double-gate structure SWCNT TFTs for (a) Device A and (b) Device B at various pH buffer solutions.

Meanwhile, pH sensing using ISFET causes unexpected instability problems such as hysteresis and drift effects. Hysteresis effect is caused by internal defective sites of sensing membrane. Fig. 3(a) shows pH change as a function of time, in a pH = 7→10→7→4→7. The hysteresis voltages of the first and last points in the pH loops of device A and B are 130 and 140 mV, respectively. The drift effect is caused by slow chemical reactions between the electrolyte surface and the sensing membrane, which changes the dielectric constant of the insulator surface and changes the capacitance of the entire insulator.

Fig. 3(b) shows the drift characteristics measured at pH 7 for 10 hours. The reference voltage change (ΔVR) represents the long-term stability of the sensor, and device A and B operate reliably with a drift rate of 72.44 and 74.42 mV/h, respectively.

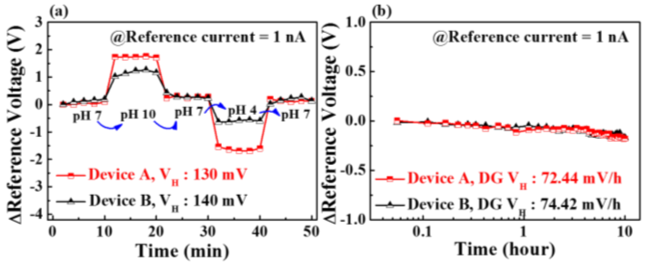

Fig. 3 (a) Hysteresis effect and (b) drift effects of the double-gate structure CNT TFTs with different bottom-gate oxide.

3. Conclusions

We fabricated a highly sensitive SEG-ChemFET sensor based on a double-gate structure scSWCNT TFTs with an engineered gate oxide and measured the sensitivity to various pH solutions. As the capacitive coupling between the engineered bottom-gate oxide (Ta_2O_5/SiO_2) and the low-k SOG top-gate oxide is increased, the sensitivity is increased and the stability of the TFT operation is improved by the passivation effect of the scSWCNT channel layer. The fabricated scSWNT ChemFET sensor has 365.65 mV/pH sensitivity, which is much higher than the Nernst limit (59.5 mV/pH), and drift rate of 72.44 mV/h. Therefore, we expect that the proposed sensor will be applicable to high-sensitivity aqueous chemical sensor and biosensor.

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