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Highly sensitive double-gate thin-film transistor pH sensors with solution-processed carbon-nanotube networks channel and AlO_x gate insulator

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Abstract

We fabricated single-walled carbon-nanotube (SWNT) networks channel thin-film transistors (SWNT-TFTs) with double-gate structure for a high sensitivity pH sensor. The SWNT channel layer and top gate AlO_x insulator were formed using a solution-based process. In order to prevent the damage of SWNT channel layer by post-deposition annealing (PDA) processes and to improve the electrical characteristics of SWNT -TFTs, microwave irradiation (MWI) was applied as a low temperature process. A very thin SWNT channel of ~1 nm thick maximized the capacitive coupling effect between the top and bottom gate oxides, resulting in pH sensitivity far exceeding the Nernst limit (59.5 mV/pH). The fabricated SWNT-TFTs pH sensor showed a sensitivity of 12.623 V/pH and a linearity of 98.87% in DG-mode. Therefore, double-gate SWNT-TFTs using high-k top gate insulators are expected to be a useful method for high-sensitivity biosensor applications.

1. Introduction

Carbon nanotubes (CNT) have unique characteristics of structural, electrical and mechanical characteristics [1]. In particular, semiconducting single-walled carbon-nanotube (SWNT) have the advantage of high transconductance owing to their high carrier mobility compared with silicon based transistor [2]. These advantages give the high charge sensitivity to the living biological molecules sensing [3]. Meanwhile, directly exposed CNT sensing membrane caused instability problems. The stability could be achieved by passivation process such as chemical vapor deposition (CVD), atomic layer deposition (ALD) or annealing metal material after e-beam deposition on CNTs. However, these processes are expensive and time-consuming. In addition, plasma or thermal damage weakens CNT properties. Therefore, the passivation method of CNTs requires a non-plasma process and a low temperature process. Meanwhile, FET-based ion sensing sensors (ISFETs) are recognized as powerful tools for biological analysis. However, the conventional ISFETs sensitivity is limited to 59.5 mV/pH (Nernst sensitivity) at room temperature [4]. This is a problem in detecting biological materials with very small potentials. To solve this problem, the sensitivity of the sensor must be increased and the capacitive coupling induced between the top- and bottom-gate oxides is considered an efficient way to easily overcome the Nernst limit [5, 6].

In this experiment, we fabricated a double gate TFT pH sensor using solution-based AlO_x as the top gate oxide and SWNT as the channel. The solution-based high-k insulator acts as a passivation layer to prevent CNT damage by plasma or heat treatment processes when forming a gate insulator. It also provides a double gate structure of the SWNT-TFT sensor, enabling capacitive coupling effects and amplifying the pH sensitivity.

2. General Instructions

Fabricated SWNT solution (semiconductor SWNT Iso-Nanotube-S, Nanointegris, USA) contains 95% of semiconducting SWNT. SWNT powder of 0.3 mg was dissolved in 30 ml of 1-methyl-2-pyrrolidinone (NMP:99+%, Sigma Aldrich) and sonicated for 2.5 h using bath-type sonicator and centrifuged at 13,000 rpm. A heavily doped p-type Si substrate with a 700 nm thermal oxide layer was immersed in 2.5 mM 3-aminopropyltriethoxysilane (APTES) diluted in distilled water for 30 m, and the SWNT solution was then spin-coated at 4000 rpm for 120 s and dried in a drying oven at 70 ℃ for 1.5 h. The thickness of fabricated SWNT networks layer was about 1 nm. The source and drain electrodes were formed by a lift-off method after deposition of 100-nm thick Ti layer with an e-beam evaporator. The active layer of SWNT was defined by O_2 plasma etching for 30 seconds. Subsequently, the AlO_x solution (Kojundo Co., Ltd) was spin-coated at 6000 rpm for 30 s to form a high-k gate insulator, and the impurities and defects in the AlO_x film were removed using MWI at 1000 W for 60 s as a low temperature PDA method to improve the electrical properties. Finally, a 150-nm thick Ti top gate electrode was formed by e-beam evaporation and lift-off method, and S/D contact holes were etched with a 30:1 buffered oxide etchant (BOE). Fig. 1 shows a schematic diagram of fabricated double-gate structure SWNT-TFTs.

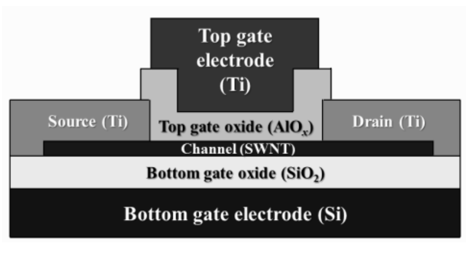

Fig. 1 Schematic structure of fabricated double-gate SWNT-TFTs.

Additionally, a separative extended-sensing gate (ESG) with a ion sensitive membrane was fabricated and connected to the SWNT-TFTs. The extended sensing gate was fabricated by depositing a 150-nm-thick ITO film and a 50-nm-thick SnO_2 film on a glass substrate by RF magnetron sputtering and attaching a PDMS reservoir. The ESG containing the pH buffer solution was then connected to the top gate of TFTs to monitor the surface potential. All electrical measurements were performed using an Agilent 4156B Precision Semiconductor Parameter Analyzer and in the shielded dark box to avoid external effects such as noise signals or light. In the double-gate structure as shown in Fig. 1, a unique series capacitor consisting of top-gate oxide/ channel/bottom-gate oxide is formed by capacitive coupling effect [5-8]. In this case, each surface potential is influenced by the opposite surface potential. In the fully depleted channel, the relationship between the threshold voltages according to the capacitance of each part is as follow [6-8]:

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

where ΔV^{B}_{th} is threshold voltage shift of bottom-gate sweep, ΔV^{T}_{th} is threshold voltage shift of top-gate sweep and C_{TG}, C_{BG} and C_{CNT} are top-gate oxide, bottom-gate oxide and the SWNT channel capacitances per unit area, respectively. Then, due to the channel top and bottom capacitance difference, the DG-mode sensing can achieve higher threshold-voltage shift (i.e., sensitivity) than the SG-mode sensing.

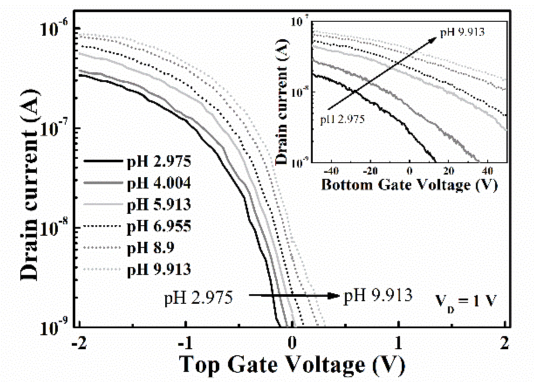

Fig. 2 Transfer curves of SWNT pH sensors for SG-mode and DG-mode (inset) operation in various pH buffer solutions.

Fig. 2 shows the transfer curves for SWNT pH sensors under SG-mode and DG-mode (inset) operations for various pH buffer solutions. Sensitivity and linearity in SG-mode were 47.95 mV/pH and 99.48%, respectively. On the other hand, the sensitivity and linearity in DG-mode are 12.623 V/pH and 98.87%, respectively. As a result, the SWNT pH sensor in the DG-mode showed higher pH sensitivity and amplification effect than the conventional Si or IGZO-based double gate structure [6-8]. The DG-mode sensitivity of SWNT pH sensor was enormously amplified about 263 times than the SG-mode due to the capacitive coupling effect. Therefore, we can conclude that capacitive coupling effect occurs in SWNT-TFTs with double-gate structure, and SWNT network with a very thin channel thickness of approximately 1 nm is advantageous for implementing high-performance sensor.

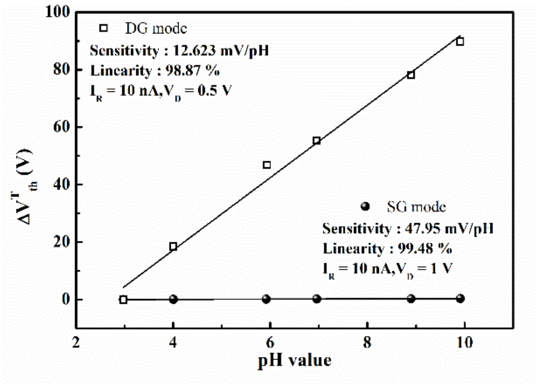

Fig. 3 Sensitivity and linearity of SWNT pH sensors for SG-mode and DG-mode in various pH buffer solutions.

3. Conclusions

We fabricated double-gate structure SWNT-TFTs and measured the sensitivity to various pH buffer solutions. We adopted a solution-based AlO_x film as the top gate insulator of the SWNT network channel and performed a low-temperature heat treatment using the MWI PDA process. These processes enable the fabrication of SWNT-TFTs with a double gate structure that is simple, inexpensive, and stable operation without damaging the SWNTs channel layer. The fabricated SWNT-TFT pH sensor showed a sensitivity of 12.623 V/pH and a linearity of 98.87% in DG-mode. In addition, very thin SWNT channels of 1-nm-thick maximized the capacitive coupling effect between the top and bottom gate oxide, resulting in pH sensitivity well beyond the Nernst limit (59.5 mV/pH). Therefore, double-gate SWNT- TFTs using high-k top gate insulators are expected to be a useful method for high-sensitivity biosensor applications.

Acknowledgements

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