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A role of silica nanoparticles in layer-by-layer self-assembled carbon nanotube and In_2O_3 nanoparticle thin-film pH sensors: Tunable sensitivity and linearity

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ABSTRACT

A role of the dielectric silica nanoparticle (SiO_2 NP) in nanomaterial chemoresistors and ion-sensitive field-effect transistors (ISFET) is demonstrated in this study. Single-walled carbon nanotubes (SWCNT) and indium oxide nanoparticles (In_2O_3 NP) are layer-by-layer self-assembled alternately with oppositely charged polyelectrolytes, respectively. Nanomaterial multilayer thin-film is patterned using photolithography and electrochemically characterized in various pH buffers. The pH sensors are implemented as resistor and transistor in absence and presence of SiO_2 NP layer. We observed tunable sensitivity and linearity of output current flowing through the conducting channel in SWCNT chemoresistor and ISFET. The role of SiO_2 NP is proven to modulate and linearize the sensitivity to pH. The linearization is attributed to a positive shift in pH gating voltage in p-type semiconducting SWCNTs. On the other hand, a tunable sensitivity is observed whereas the linearization is not demonstrated in In_2O_3 NP ISFETs. The increased sensitivity with SiO_2 NP in acidic region is caused by a positive shift in gate voltage due to the protonation of the surface hydroxyl groups. This facile modulation and linearization of the electrochemical sensitivity in semiconducting nanomaterial thin-film device by means of the additional SiO_2 NP layer is useful for developing various functional nanomaterial-based biosensors.

1. Introduction

The nanomaterial is a good candidate for developing solid-state pH electrode due to the unique electrochemical property. A series of nanomaterial-based ion-sensitive field-effect transistors (ISFET) was reported as pH [1,2] and acetylcholine sensors [3,4] possessing silica nanoparticles (SiO_2 NP) as a dielectric layer on top of semiconducting nanomaterial thin-film. The authors argued that SiO_2 NPs acted as a gate dielectric layer in the conventional FET structure. However, the self-assembled SiO_2 NP thin-film is porous, so that it could not prevent the analyte solution penetrating into the semiconducting layer perfectly as in conventional ISFETs. In consequence, it is questionable whether the chemical information such as pH or analyte concentration is transformed only through semiconducting layer or together with SiO_2 NP layer. In addition, single-walled carbon nanotube (SWCNT) thin-film without any dielectric layer showed the pH-sensitive electrochemical properties [5], since the proximal ionic composition change [5–7] and protonation/deprotonation of the surface functional groups of semiconducting nanomaterials [8,9] influence the electrical properties of nanomaterial thin-film itself. This suggested the elimination of gate dielectric layer. Therefore, the reason for the existence of SiO_2 NP layer in all-nanomaterial ISFETs has not been elucidated so far.

In case of the conventional ISFET with a dielectric, pH decrease in sample solution induces more positive charges on the dielectric due to the protonation of surface hydroxyl group. This plays the role of positive shift in the gate voltage, resulting in decreasing conductance in p-type semiconducting material in a sense of conventional FET. However, SWCNT ISFET with porous SiO_2 NP layer actually showed the opposite behavior, which was linearly increasing conductance with decreasing pH [2]. It meant the protonation/deprotonation of carboxylic groups on SWCNTs played a dominant role to determine the overall behavior that was decreasing conductance with pH [8]. On contrary, the penetration of the sample solution might be beneficial to n-type semiconducting materials, e.g. indium oxide (In_2O_3) nanoparticles [1], since the gate voltage shift by SiO_2 NP layer is positive. Nonetheless, this dual effect of solution pH on the conductance of semiconducting nanomaterials in the presence of SiO_2 NPs makes it difficult to estimate the electrochemical behavior of nanomaterial devices, exploit excellent properties, and design novel nanostructures that might have a higher performance.

Although much effort has been made on demonstrating biosensing applications of nanomaterials, no systematic study has been

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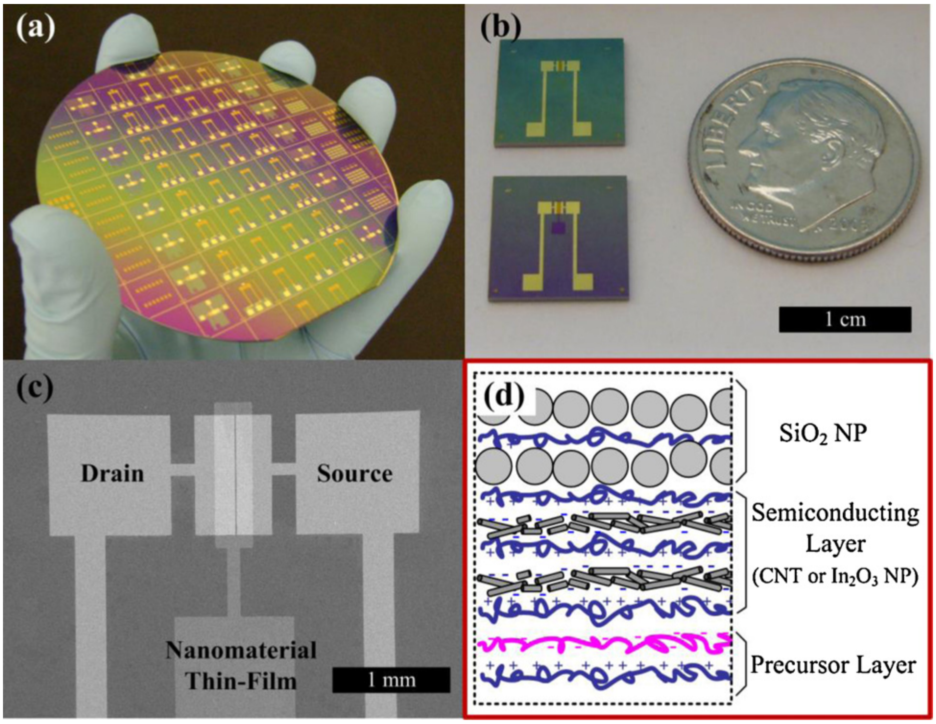

Fig. 1. Layer-by-layer self-assembled nanomaterial thin-film pH sensors: (a) 4 in. wafer scale fabrication, (b) diced individual sensing chips in size of 1 cm by 1 cm, (c) SEM image of the electrode patterns and nanomaterial thin-film, and (d) hierarchical structure of nanomaterial thin-film composed of precursor layer of $(PDDA/PSS)_2$, semiconducting layer of SWCNT or In_2O_3 NP film, and silica nanoparticle layer.

reported yet regarding the electrochemical pH transducing properties of nanomaterial thin-film. We demonstrate in this report that pH sensitivity of the nanomaterial thin-film chemoresistor and ISFETs is tunable simply by depositing SiO_2 NP layer on top of semiconducting nanomaterial multilayer fabricated by layer-by-layer (LbL) self-assembly. We used the thin-film of SWCNTs and In_2O_3 NPs as a semiconducting nanomaterial. A new analysis on the pH-dependent conductance of SWCNT and In_2O_3 NP chemoresistors and ISFETs was performed, and the role of SiO_2 NPs layer was elucidated. Finally, we showed that the role of SiO_2 NPs in both SWCNT chemoresistors and ISFETs is to tune and linearize the pH sensitivity without complex wet chemistry. Although the linearization was not observed in In_2O_3 ISFETs, the tunable sensitivity with SiO_2 NPs particularly in acidic region was clearly demonstrated. The SiO_2 NP layer on top of the semiconducting layer plays the role of the charge collector, influencing the conductance of the semiconducting layer. In conjunction with a facile integration of SiO_2 NP, the tunable electrochemical properties of nanomaterial thin-film could be used for developing a variety of electrochemical biosensors.

2. Experiments

2.1. Materials

SWCNT (purity: 90% of SWCNT and 95% of CNT, diameter: 1–2 nm, length: 5–30 μm, SSA: 300–380 m^2/g) was purchased from Nanostructured & Amorphous Materials, Inc. and chemically functionalized in concentrated acids as done previously [6,10]. The resulting aqueous SWCNT dispersion had the final concentration of 0.6 mg/ml and pH of 5.5. In_2O_3 particle (In_2O_3 NP), aqueous polydiallyldimethylammonium chloride (PDDA, M_w = 200–350k) and sodium polystylenesulfonate (PSS, M_w = 70k) were obtained from Sigma–Aldrich. In_2O_3 NPs were dispersed into 12 mM HCl (pH 3.9) aqueous solution with a concentration of 50 mg/ml. PDDA and PSS were diluted to have a concentration of 1.4 and 0.3 wt%, respectively, with 0.5 M sodium chloride (NaCl). Another set of PSS solution (PSS2) was prepared by adjusting the pH of PSS solution to 3.9 using HCl to preserve the surface charge of In_2O_3 NPs in the PSS2 solution. As-received colloidal silica nanoparticles (SNOWTEX®-XL, Nissan Chemical America Corp.) of 4 g was diluted to 100 mL of deionized water (DIH_2O) resulting in a concentration of 16 mg/ml with pH 7.0. The pH buffers were formulated using $NaH_2PO_4{\cdot}H_2O$ and $Na_2HPO_4{\cdot}7H_2O$ so that the resulting pH ranged from 5 to 9, which was targeted for biosensing application.

3. Device fabrication

Nanomaterial thin-film devices were fabricated following the procedure previously reported [5,8]. Chromium (Cr, 300 Å) and gold (Au, 1000 Å) were electron-beam evaporated on a 4 in. silicon wafer with thermally grown oxide 2 μm thick. Photolithography was used to fabricate source and drain electrodes. The conducting channel dimension was 1 mm wide and 10 μm long. Another lithographic patterning was performed for lift-off mask layer of photoresist in order to confine nanomaterial thin-film on the conducting channel. O_2 plasma at a power of 100 W and O_2 flow rate of 100 sccm was applied for 1 min to change the surface hydrophilic for the subsequent assembly of nanomaterials. Then, LbL assembly of nanomaterials was conducted on the wafer scale under atmospheric pressure and room temperature. SWCNT was assembled alternately with positively charged PDDA following a sequence of $[\text{PDDA (10 min)} + \text{PSS (10 min)}]_2 + [\text{PDDA (10 min)} + \text{SWCNT (15 min)}]_5$. On the other hand, In_2O_3 NPs were assembled alternately with PSS2 with a sequence of $[\text{PDDA (10 min)} + \text{PSS (10 min)}]_2 + [In_2O_3\text{ NP (14 min)} + \text{PSS2 (10 min)}]_5$. Two kinds of nanomaterial thin-film were covered with the additional dielectric layer of $[\text{PDDA (10 min)} + SiO_2\text{ NP (4 min)}]_6$ to compare the electrochemical sensitivity to pH buffers in the absence and presence of silica nanoparticles. Two bilayers of (PDDA/PSS) were to enhance the surface charge for functional