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Abstract

Polymer-Mediated Increase in Sensitivity and Stability of CNT-FET pH Sensor †

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Abstract: There has been an increasing interest in pH sensors based on nanomaterials in environmental and biological sensing. This work addresses persistent challenges in the development of stable and sensitive pH measurements. We present a CNT-FET-based pH sensor with a hybrid encapsulation stack consisting of poly(4-vinylpyridine)/HfO_2 layers. The resulting liquid-gated sensors feature an excellent sensitivity of up to 50 mV/pH in an operation regime below 1 V, which is within the electrochemical window of most biological species. Moreover, the P4VP encapsulation results in a 1000× higher on-off-current ratio and nearly 83% smaller drift compared to devices encapsulated in only HfO_2.

Keywords: pH sensor; CNT-FET; wafer-level fabrication; poly(4-vinylpyridine); HfO_2

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1. Introduction

In ion-sensitive field-effect transistors (FETs), pH- or biosensors measure the variation of surface charges and modulate the device current. The concentration of the surface charges and, e.g., a pH value, can be determined by measuring the device current [1]. Nanomaterials, such as carbon nanotubes (CNTs), have been explored in FETs for their applications in enhancing sensing capabilities and sensitivity due to their atomically thin body thickness [2]. However, to operate CNT-FETs in a liquid environment, they need an encapsulation layer to reduce drain and gate leakage currents, protect against electrical stress upon long-time measurements, and reduce device drift [3]. For biosensors, often very thin high-κ materials such as HfO_2 are used to account for the Debye length in the nm range that defines the ion-sensitive distance of the FET [4]. Here, we present the wafer-level compatible fabrication and sensor characteristics of a pH-sensitive carbon nanotube-based field-effect transistor. Furthermore, we improved the device characteristics with the addition of a poly(4-vinylpyridine) (P4VP) encapsulation novel for CNT-FET pH sensors. P4VP is a pH-responsive polymer and acts as a highly efficient protection against unintended doping effects, providing enhanced electron transfer kinetics and higher device stability [5].

2. Materials and Methods

The sensors were fabricated on a highly doped Si/SiO_2 wafer with an HfO_2 deposited on top via atomic layer deposition. The semiconducting single-walled-CNTs were integrated from a dispersion (Nanointegris IsoSol-S100) via a printing technique and patterned using oxygen plasma etching. Subsequently, the CNTs were contacted using e-beam lithography, ion-beam sputter deposition of $Cr/Pt/Al_2O_3$, and a lift-off procedure. After annealing, the FETs were encapsulated with 5 nm HfO_2. To access the local liquid gate through the backside of the wafer, wet etching was used for opening contacts to Si. These areas were then covered with Cr/Pt. For the passivation of the source and drain electrodes, locally structured OiR906-12i optical resist was used. The wafer's backside is scratched, and Al is deposited via physical vapor deposition for electrical contact. On the final device, the P4VP-isopropanol solution was spin-coated as described in [6]. Next, 4X saline-sodium citrate (SSC) buffer solutions with pH adjusted to 5 and 9 were used for the pH sensing experiments. A PDMS liquid cell was placed on top of the sensor for the liquid measurements, and the buffers were continuously delivered into the microchannel. The pH solutions act both as the media for the pH sensor measurements and for the electrolyte gating due to the presence of charged species. In Figure 1a, one can observe the structure of the final device, with ~12 nm P4VP.

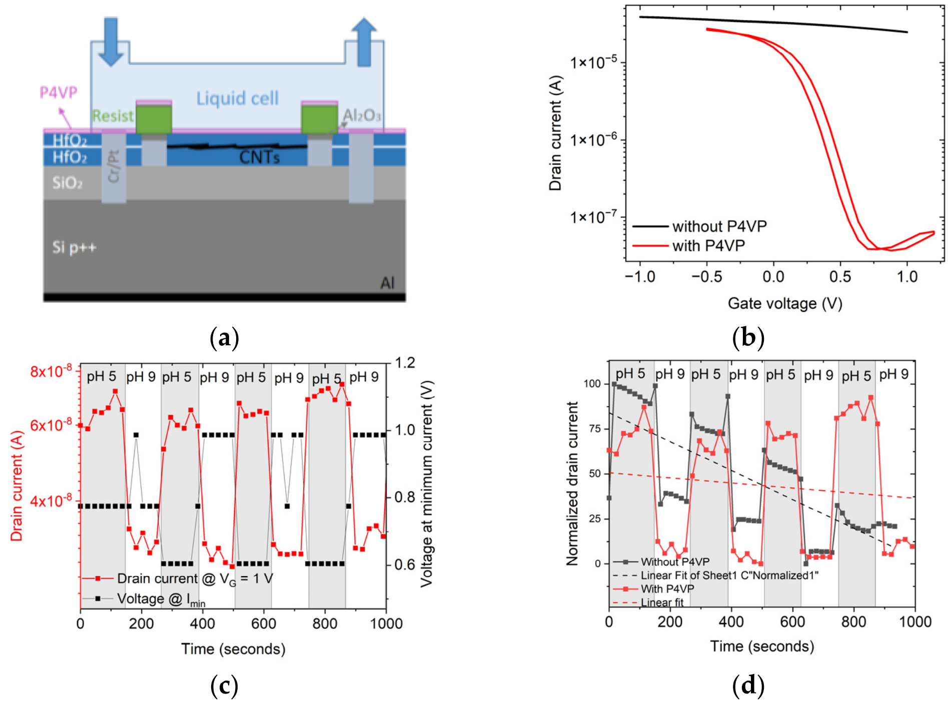

Figure 1. (**a**) Sketch of CNT-FET with P4VP passivation and liquid cell on top. (**b**) Transistor curves with and without P4VP encapsulation were measured in a buffer solution with a pH of 5. (**c**) Time evolution of the voltage at the minimum current and the drain current upon pH stimulus measured at a gate voltage of 1 V for the P4VP modified transistor. (**d**) The normalized current of the P4VP encapsulated and not-encapsulated sensors upon pH stimulation at a gate voltage of 1 V, including a linear fit for the drift determination.

3. Discussion

The transistor characteristics of the P4VP-encapsulated and not-encapsulated sensors are shown in Figure 1b. One observes that the presence of P4PV caused a significant modification in the electrical behavior, such as the 1000× improvement of the on-off-current ratio and the shift of the operation point (e.g., the minimal current point) to below 1 V. This operation range fits the electrochemical window of most biological species, thus, it is highly beneficial for developing biosensor applications. Buffer solutions with pH values of 5 and 9 were alternatingly introduced into the channel and the transistor characteristics were measured, to monitor the drain current modulation. In Figure 1c, one can observe the evolution of the voltage for the minimum current and the drain current for the P4VP/HfO_2 encapsulated device. The voltage modulation upon different stimuli returned a sensitivity of 50 mV/pH unit and a similar behavior was followed in terms of the drain current. Comparing both devices upon pH stimulation, as shown in Figure 1d, the P4VP-modified transistor shows an 82.5% smaller drift, while maintaining a lower gate leakage current.

We expect the P4VP to have different effects. On one hand, the resist-passivated electrodes suffer under well-known delamination effects that can result in electrochemical side reactions and enhanced drain leakage currents, which can be compensated for with a P4VP coating. On the other hand, P4VP improves the gate field coupling to the CNTs by eliminating the doping effect in small CNT bundles [6]. Moreover, the polymer prevents the accumulation of charged species in the channel area, which could mitigate the faster aging of the transistor and electrical stress, generating the current drift [3]. Lastly, the spin coating process for P4VP encapsulation offers highly compatible processing in terms of fab manufacturing.

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