High Sensitivity of Dry-Type Nanowire Sensors With High-k Dielectrics for pH Detection via Capillary Atomic Force Microscope Tip Coating Technique

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***Abstract*—Dry-type poly-Si nanowire pH sensors with high-k dielectrics have been demonstrated with the aid of novel focus ion beam engineered capillary atomic force microscopy (C-AFM) tip. By means of this C-AFM tip coating technique, the relatively few testing solutions can be transferred onto the surface of a nanowire, preventing the sensor device from the immersion in the liquid and therefore suppressing the possible leakage current from the testing solution. As compared with the TEOS SiO$_2$, the pH sensors comprising Al$_2$O$_3$, TiO$_2$, and HfO$_2$ high-k materials exhibit the better sensitivities due to their enhanced capacitances. The best sensitivity (138.7 nA/pH) and linearity (99.69%) for a HfO$_2$ dielectric can be ascribed to the higher k value and larger bandgap with respect to the Al$_2$O$_3$ and TiO$_2$, accordingly. Consequently, the C-AFM tip coating technique incorporating with HfO$_2$ dielectric suggests the potential for the detection of a minute quantity of biomedicines.**

***Index Terms*—High-k dielectrics, nanowire, pH sensor.**

I. INTRODUCTION

THE ion-sensitive field-effective transistor (ISFET) is one of the most popular biochemical sensors due to its small size, fast response time, high input impedance, and high compatibility with the commercial CMOS process [1]. The device structure of ISFET is directly descended from the conventional MOSFET by exposing the gate dielectric to an electrolyte solution. Thus, the charged ions that are bound on the sensing membrane give rise to change the surface potential of the silicon channel, which in turn modulates the conduction current of the sensor device. Since the ISFET is wetted under the electrolyte solution, isolating the electrical contacts between the source and drain to improve the sensing accuracy has become one of the important challenges. In addition, the device encapsulation of ISFET often causes a series of troubled assembly processes, leading to a high-failure risk [2]. Therefore, for reliable measurement, it is necessary to develope a dry sensing environment which can immunize against the possible leakage current from the testing solution. Herein, we demonstrate a dry-type poly-Si nanowire pH sensor coated with high-k dielectrics to improve the sensing performance. A focus ion beam (FIB) process was used to create a small groove on the atomic force microscope (AFM) tip to load and transfer the relatively few testing solutions on the surface of poly-Si nanowire sensors via the capillary phenomenon. In addition to the advantages of preventing the sensor devices from immersion in the liquid, the pH sensors based on a nanowire structure can be applied to realize the ultrasensitive detection capability for the minute quantities of analytes by means of the inherent large-surface-area-to-volume ratio. Furthermore, the introduction of high-k dielectrics enables the charged ions that are bound on the sensing membranes to effectively modulate the channel conductivity, resulting in a higher pH sensitivity.

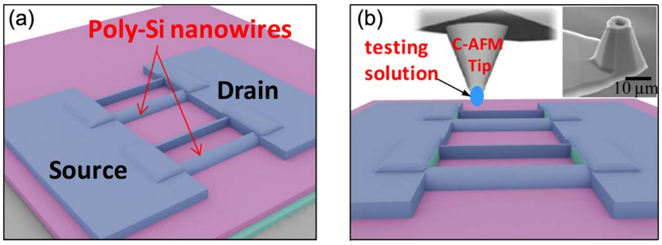

Fig. 1. Schematic plots of the key steps for dry-type poly-Si nanowire sensor. (a) Nanowire structure was formed after the removal of the 100-nm-thick TEOS oxide strips. (b) PBSs with different pH values were loaded in the C-AFM tip and then delivered on the poly-Si nanowires during the AFM scanning. The inset shows the C-AFM tip after the FIB milling process.

II. DEVICE FABRICATION

Based on the earlier works, the dry-type poly-Si nanowire pH sensors were fabricated via a sidewall spacer technique, as shown in Fig. 1 [3], [4]. A 1.0-μm-thick thermal SiO$_2$ was first grown on the p-type silicon wafers. Then, a 50-nm-thick Si$_3$N$_4$ and a 100-nm-thick TEOS SiO$_2$ were sequentially deposited through low-pressure chemical vapor deposition as the etch-stop layer and the sacrificial layer, respectively. Next, the sacrificial SiO$_2$ layer was etched as several dummy strips by the reactive ion etch process, followed by a layer of 100-nm-thick amorphous silicon film deposited at a temperature of 550 °C and doped by phosphorous ion implantation at 40 keV to a dose of 5×10^{15} cm^{-2}. After the source/drain (S/D)-pad lithography and dry etching process, the device active region with narrow a-Si sidewall nanowires that naturally connected to the broad S/D pad was obtained. The a-Si sidewall

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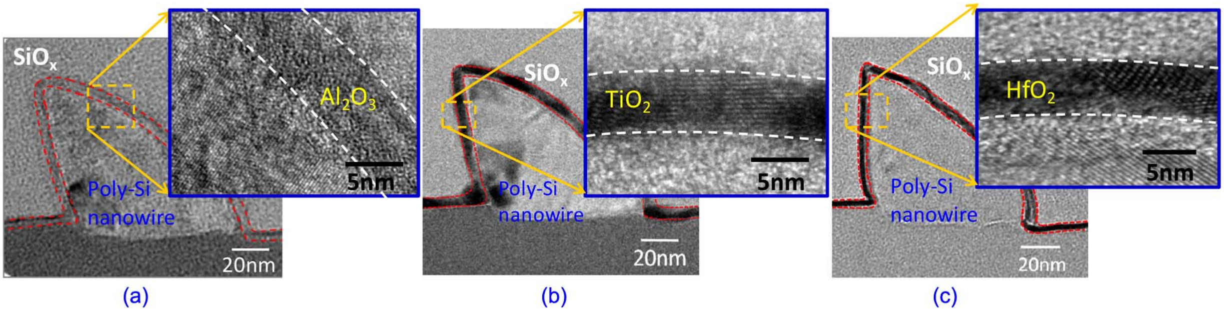

Fig. 2. XTEM images of poly-Si nanowires with (a) Al_2O_3, (b) TiO_2, and (c) HfO_2 high-k dielectrics.

nanowires were then transferred to poly-Si by solid-phase crystallization at 600 °C for 24 h in N_2 ambient. Afterward, the diluted HF solution was used to etch off the sacrificial SiO_2 to form the poly-Si nanowires, as shown in Fig. 1(a). The 5-nm-thick high-k dielectrics of Al_2O_3, TiO_2, or HfO_2 were then deposited onto the poly-Si nanowire surface by an atomic-layer-deposition system at 250 °C, followed by a rapid thermal annealing (RTA) process at 900 °C for 30 s in N_2 ambient. Next, a γ-APTES layer was coated on the high-k dielectric layers as sensing membrane utilizing the capillary AFM (C-AFM) tip [5]. While beginning the sensing process, the phosphate buffer solutions (PBSs) with different pH values were loaded in the C-AFM tip and then delivered on the poly-Si nanowires during the AFM scanning in the contact mode, as shown in Fig. 1(b). The inset plot of Fig. 1(b) shows the scanning electron microscopy image of the C-AFM tip possessing a groove with 2.5 μm in diameter and 4 μm in depth after the FIB milling process. The current variation magnitude of poly-Si nanowires, $\Delta I = I$ (after dropping PBSs) $-I$ (before dropping PBSs), was measured by the semiconductor analyzer Agilent 4156 C. The poly-Si nanowire sensor with a TEOS SiO_2 dielectric was also fabricated for reference.

III. Results and Discussion

The pH sensors with two nanowires of 0.5 μm in channel length are employed in this work. Fig. 2(a)–(c) shows the cross-sectional transmission electron microscopy (XTEM) images of poly-Si nanowires with Al_2O_3, TiO_2, and HfO_2 thin films, respectively. According to the high-resolution XTEM, the physical thickness of each high-k dielectric is approximately 5 nm, and the Al_2O_3 is amorphous phase, while the TiO_2 and HfO_2 thin films are polycrystalline after the RTA process. Fig. 3(a)–(d) shows the measured I–V characteristics of poly-Si nanowires before and after PBS droppings with pH = 5.0 for the TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 dielectric layers, respectively, and the channel current variations ΔI at $V_{\mathrm{DS}} = 5$ V are 78.2, 201.2, 247.4, and 296.9 nA, accordingly. As compared with TEOS SiO_2, the poly-Si nanowires with high-k dielectrics exhibit greater current variation magnitudes, suggesting that the channel conductivity can be effectively modulated by the introduction of high-k materials. The sensitivities of poly-Si nanowire pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 dielectrics are shown in Fig. 4 in the range of pH 4–10. The pH sensitivity values are extracted as 29.0, 94.0, 115.6, and 138.7 nA/pH, respectively, while the linearities are 99.43%, 99.57%, 99.64%, and 99.69% with respect to the dielectric layers of TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2, accordingly. The high-k dielectrics present the better pH response than the conventional TEOS SiO_2. Based on the device physics of an electrolyte–insulator–semiconductor field-effect transistor [6], the drain current–voltage characteristics can be expressed by

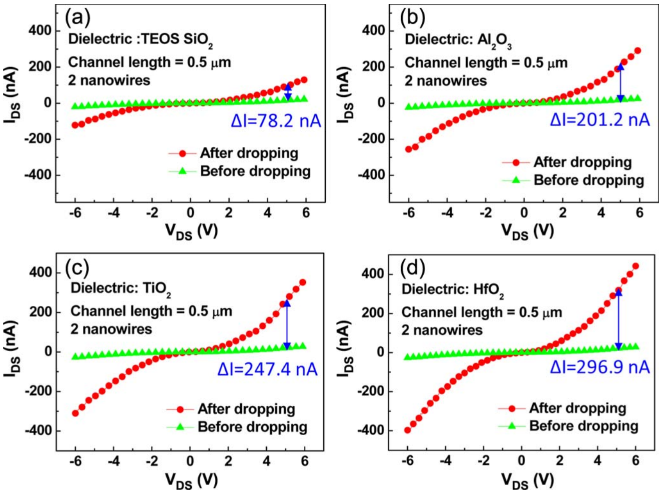

Fig. 3. I–V characteristics of poly-Si nanowires before and after PBS dropping for (a) TEOS SiO_2, (b) Al_2O_3, (c) TiO_2, and (d) HfO_2 dielectrics.

$$I_D = \frac{W}{L}\mu_n^* C_o \left\{ \left[\phi_0 - \phi_{0(\mathrm{FB})} - 2\phi_F - \frac{V_{\mathrm{DS}}}{2} \right] V_{\mathrm{DS}} - \frac{2}{3}\frac{\sqrt{2\varepsilon_s \varepsilon_0 q N_A}}{C_o} \left[(V_{\mathrm{DS}} + 2\phi_F)^{\frac{3}{2}} - (2\phi_F)^{\frac{3}{2}} \right] \right\}$$

where the ϕ_0 is the insulator surface potential which is related to the semiconductor surface charge (Q_S) and semiconductor surface potential (ϕ_S) by

$$\phi_0 = \phi_s + \phi_{0(\mathrm{FB})} - \frac{Q_s}{C_o}.$$

It should be noted that the drain current–voltage characteristics relied critically on the insulator capacitance C_o and semiconductor surface potential ϕ_S. Owing to the enhanced dielectric capacitance of high-k dielectric layers, the semiconductor surface potential ϕ_S can be effectively promoted, thus remarkably improving the pH sensitivity. Among these high-k dielectrics, the HfO_2 one shows the best pH sensitivity. It is because the HfO_2 possesses the higher k value than Al_2O_3 one. Although the TiO_2 owns the highest k value, the bandgap of TiO_2

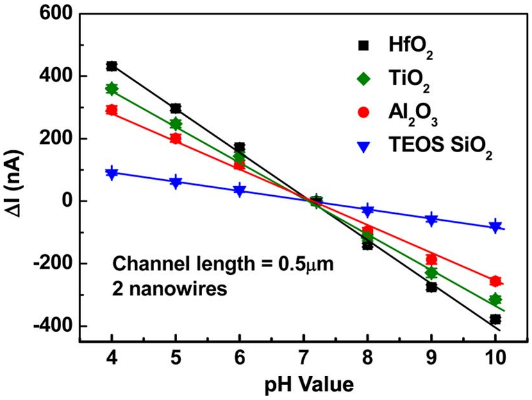

Fig. 4. Sensitivities of poly-Si nanowire pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 dielectrics.

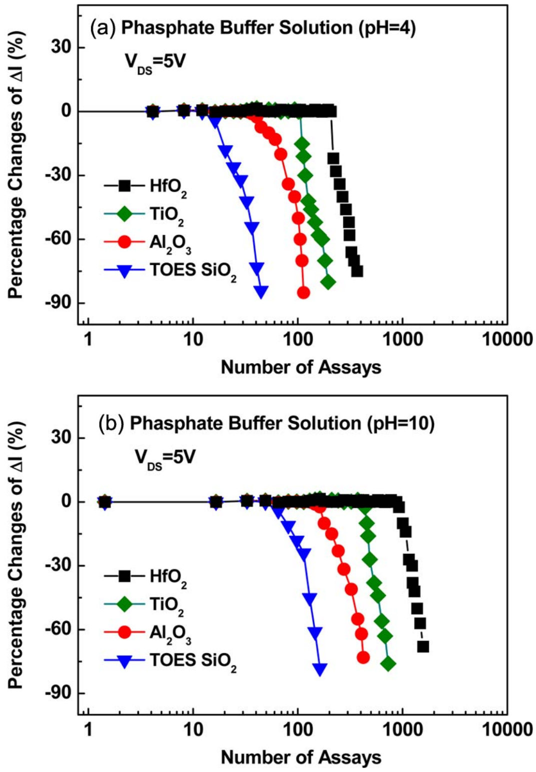

Fig. 5. Reproducibility tests of poly-Si nanowire pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 dielectrics in the PBSs at (a) pH 4 and (b) pH 10.

(3.05 eV) is smaller than that of HfO_2 (6 eV), giving rise to a smaller conduction band offset of TiO_2 with respect to Si (0.05 eV), compared to 1.5 eV for HfO_2 [6]. Since the dielectric leakage current is increased with the reduction of conduction band offset [7], [8], the leakage current of TiO_2 would be larger than HfO_2, resulting in an inferior sensing ability. The reproducibility tests of the poly-Si nanowires for pH detection are also investigated. After the first pH sensitivity detection of the sensor, the coated PBSs were removed thoroughly from the poly-Si nanowires by DI water and then dried with N_2. Next, the new PBSs with the same pH value were recoated on the surface of poly-Si nanowires and followed by the second pH sensitivity detection. The same process sequence was duplicated until the current variation value was obviously degraded. Fig. 5(a) and (b) shows the reproducibility tests of poly-Si nanowire pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 dielectrics in the PBSs at pH 4 and pH 10, accordingly. The numbers of assays before degradation are 12, 33, 106, and 208 times for a pH value of 4 and 49, 154, 420, and 919 times for a pH value of 10 with respect to the TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 dielectrics, correspondingly. Consequently, the HfO_2 sample exhibits the highest number of assay tests. It is because the HfO_2 dielectric appears the better crystallinity, giving rise to superior acid/alkali resistance ability during reproducibility tests [9]. In contrast, the TEOS SiO_2 shows the worst assay tests, indicating that the membrane can be severely harmed by ions in the testing solution [10].

IV. CONCLUSION

In this letter, dry-type poly-Si nanowire pH sensors with various high-k dielectrics have been demonstrated to enhance the sensing performance by means of the C-AFM tip coating technique. The sensing characteristics are strongly determined by the k value, bandgap, and crystallinity of dielectric membranes. The pH sensor with a HfO_2 dielectric exhibits the best sensitivity (138.7 nA/pH) with respect to TiO_2 (115.6 nA/pH), Al_2O_3 (94.0 nA/pH), and TEOS SiO_2 (29.0 nA/pH). The superior sensing ability of the HfO_2 dielectric can be explained by the higher k value than Al_2O_3 and larger bandgap than TiO_2. In addition, the HfO_2 sample also demonstrates the highest reproducibility tests due to its better crystallinity. Therefore, the unique C-AFM tip coating technique incorporating a HfO_2 dielectric featuring the excellent sensor performance is very promising for the application in detecting a minute quantity of biomedicines.

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