ECS Transactions, 45 (3) 537-542 (2012)
10.1149/1.3700918 ©The Electrochemical Society

Polysilicon Nanowire Sensor Devices Based on High-k Dielectric Membrane for pH Sensing and DNA Detection

Chun-Yu Wu[1], Po-Yen Hsu[2], Chao-Lung Wang[1], Ta-Chuan Liao[1], Huang-Chung Cheng[1], You-Lin Wu[2]

[1]Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, 1001 University Road, Hsinchu, Taiwan 300, ROC
[2]Department of Electrical Engineering, National Chi Nan University, Puli, Nantou, Taiwan, R.O.C.

The pH sensing characteristics of poly-Si nanowires with high-k sensing membranes are investigated. As a result, the sensing membrane of HfO_2 exhibits higher sensitivity and better reproducibility test as compared with TEOS SiO_2, Al_2O_3, TiO_2 films. The sensor device with HfO_2 dielectric membrane reveals a great pH sensitivity of 172.8 nA/pH. In additon, the label-free DNA detection ability of the poly-Si nanowires is also demonstrated. The 10-base-long single-strained homopolymers DNA molecule solution with an ultra-low concentration of 0.01nM can be detected by using HfO_2 sensing film. Such a poly-Si nanowires structure with HfO_2 sensing membrane is very suitable for future biochemical sensors applications.

Introduction

The ion sensitive field-effective-transistor (ISFET) is one of the most popular biochemical sensors due to their small size, fast response time, high input impedance, and high compatibility with commercially CMOS process (1). The performance of the ISFET is significatly influenced by the sensing member. For example, the SiO_2 sensing membrane have been widely applied to the detection of chemical quantities because of its easier growth and good interfaces between gate dielectric and silicon substrate. Although the SiO_2 film can be successfully used as pH-sensitive membrane, it results to poor sensitiveity of pH sensing, which has been ascribed to the low dielectric constant of 3.9. On the other hand, SiO_2 membrane is severely damaged by ions in electrolyte, decreasing the sensing accuracy for logn-term usage. Recently, the metal oxides such as Al_2O_3, HfO_2, Ta_2O_3, and WO_3 (2-5), have been considered the promising material to replace the conventional SiO_2 film due to the higher gate dielectric capactance. Introduction of high-k dielectrics make the charged ions that bound on the sensing membrane sufficiently modulate the channel current and thereby promote the sensitivity. However, to date, rare research works demonstrate such high-k dielectric on poly-Si nanowire. In this work, we propose a simple process to construct a poly-Si nanowire structure coated with various high-k sensing membranes to improve the sensor performance.

Experiments

A 1.0-μm-thick thermal SiO_2 was firstly grown on p-type silicon wafers. Then, a 50-nm-thick Si_3N_4 and a 100-nm-thick TEOS SiO_2 were sequentially deposited through the low pressure chemical vapor deposition (LPCVD) system as the etch-stop layer and the sacrificial layer, respectively. After the sacrificial SiO_2 layer was anisotropic etched by reactive ion etch (RIE) process as shown in Fig. 1(a), the 100-nm-thick a-Si film was conformal deposited by LPCVD at 550 °C. Next, the a-Si thin film was implanted phosphorous at 40 keV to a dose of 5×10^{15} cm^{-2}. After the I-line stepper photolithography and RIE process, the pairs of a-Si sidewall spacers with a source/drain pad were *in situ* resided against both sidewalls of SiO_2 dummy strips, as shown in Fig. 1 (b). The a-Si sidewall spacers were then transferred to poly-Si-type by solid phase crystallization at 600 ^{o}C for 24 h in N_2 ambient. Afterwards, the diluted HF solution was used to etch the dummy SiO_2 to fabricate the poly-Si nanowires, as shown in Fig. 1 (c) (6-8). Next, the 3-nm-thick high-*k* dielectric material HfO_2, Al_2O_3, and TiO_2 was deposited onto poly-Si nanowires surface by ALD system, followed by a rapid thermal annealing (RTA) process at 900 °C for 30 s in N_2 ambient. Based on our previous work (9), the FIB-processed C-AFM tip was used to load and transfer the γ-APTES solution on the surface of poly-Si nanowires. Finally, the sample was cured on a hot plate at 120°C for 300s. While beginning the sensing process, the phosphate buffer solutions (PBSs) with different pH-value or single-strained homopolymers DNA with different concentrations were loaded in the C-AFM tip and then scanned the poly-Si nanowire surface by AFM system (SEIKO 300 HV) of contact mode. The current variation value of poly-Si nanowire, $\Delta I = I$ (after dropping PBSs) $-$ I (before dropping PBSs), were measured by the semiconductor analyzer Agilent 4156C. For comparison, the poly-Si nanowires with TEOS SiO_2 sensing membrane were also fabricated by the same process sequence.

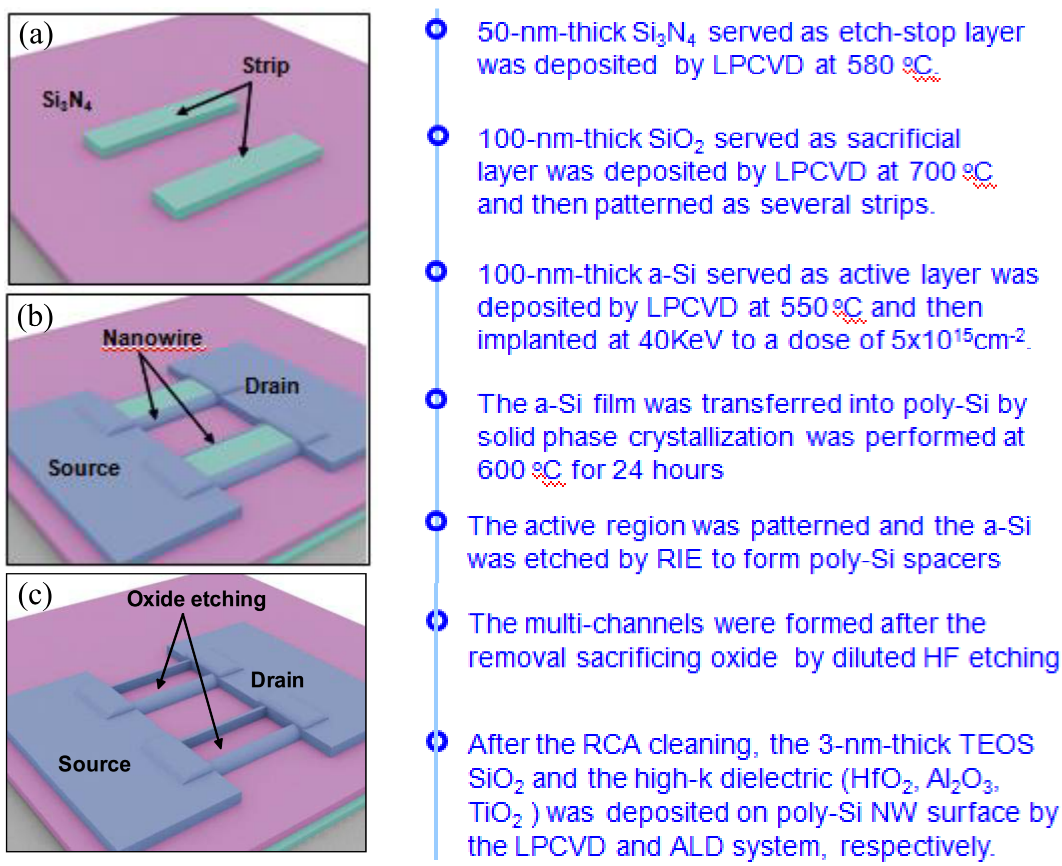


Fig.1. The schematic diagram of the key fabrication process steps of the proposed poly-Si nanowire sensor.

Results and discussion

The pH sensor with a channel length (L) of 0.5 μm was employed in this work. Fig. 2 shows the cross-sectional transmission electron microscopy (TEM) image of poly-Si nanowires with HfO_2 gate dielectric. It can be obviously found that the HfO_2 thin film is polycrystal after the RTA process. The sensitivity of poly-Si nanowires pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 sensing membranes are shown in Fig. 3. The channel current variation ΔI of poly-Si nanowire is defined at a drain-source voltage of 5 V. The pH sensitivity values were extracted as 36.1, 117.0, 143.9, and 172.8 nA/pH wtih respect to the sensing membrane of TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2, accordingly. The sensing film with higher-k value demonstrates the better pH response. According to the double-layer model (10), the pH sensitivity is strongly depended on the surface band bending and the hydrogen ion concentration. The high-k sensing membanes will cause a larger surface band bending and a higher electron density near the surface, significantly ehnanceing the channel current variation ΔI. However, the poly-Si nanowires with HfO_2 membrane shows a highest pH sensitivity although the k-value of HfO_2 (k = 25) is smaller than TiO_2 (k = 80). This can be explained by the smaller band gap and the lower band offset of TiO_2, resulting in the higher leakage current of gate dielectric.

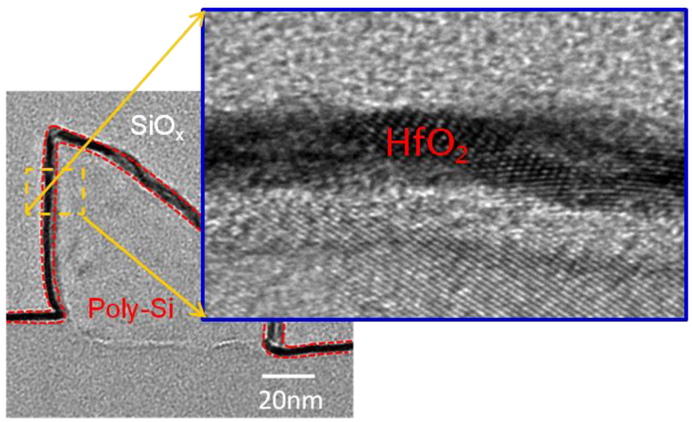


Fig.2. The cross-sectional TEM image of poly-Si nanowires with HfO_2 gate dielectric.

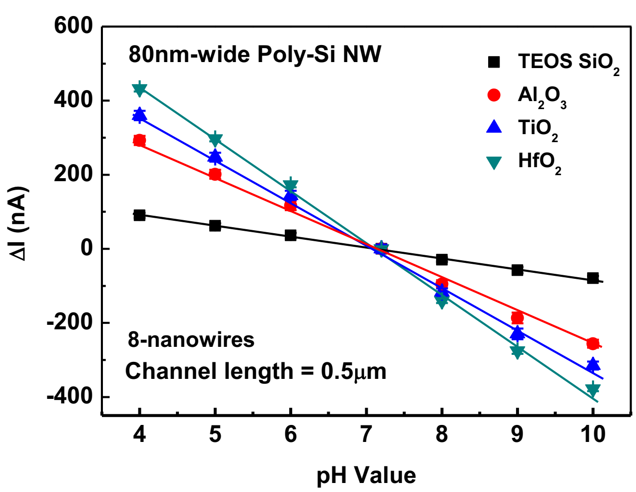
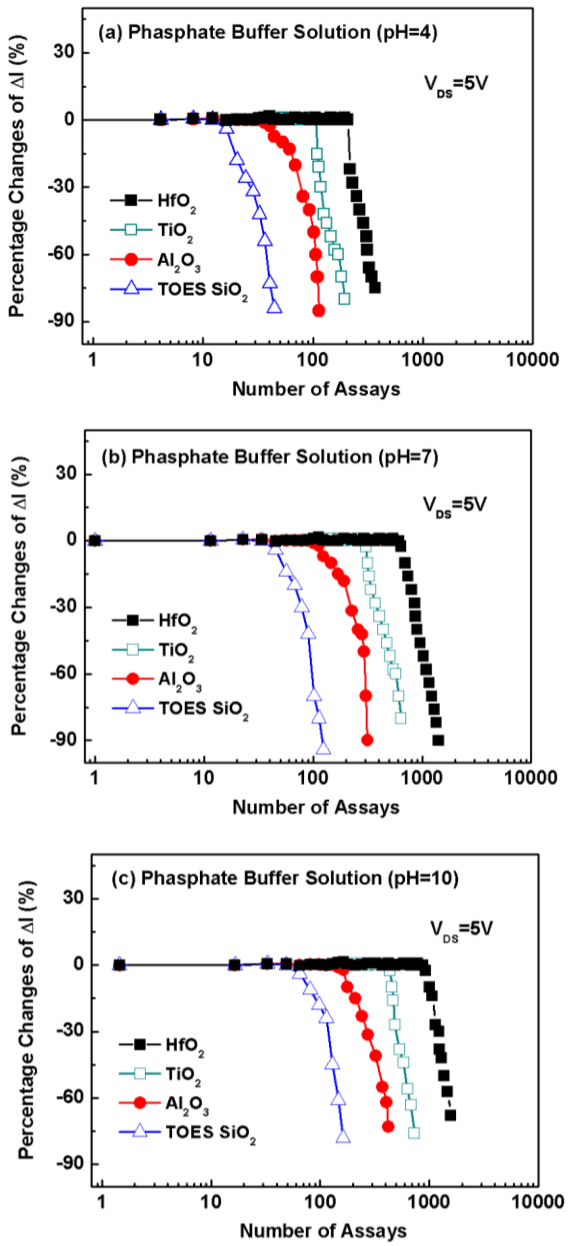


Fig. 3. The sensitivity comparison of the poly-Si nanowire sensors coated with different high-k materials and TEOS oxide.

The reproducibility tests of the poly-Si nanowires for pH detection were also investigated. After the first pH sensitivity detection of sensor, the coated PBSs was removed from the poly-Si nanowires by DI water and then dried with N_2. Next, the new PBSs with the same pH vaule were re-coated 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. Figs. 4(a)-4(c) show the reproducibility of pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 sensing membranes in pH vaule of 4, 7, and 10, respectively. From the experimental result, the poly-Si nanowires with HfO_2 sensing film reveals the highest number of assay tests. This is due to the polycrystalline structure of HfO_2 film which is difficult to remove by the wet etch process (11). Contrastively, the TEOS SiO_2 sample shows the poor reproducibility tests, indicative of the amorphous structure that can be seriously harmed by ions in electrolyte.



Figs. 4(a)-4(c) The reproducibility of pH sensors with TEOS SiO_2, Al_2O_3, TiO_2, and HfO_2 sensing membranes in pH vaule of 4, 7, and 10, respectively.

The label-free DNA detection ability of the poly-Si nanowires with HfO_2 sensing membrane is demonstrated in this work. The single-strained homopolymers, poly(T) (5'-TT...TT-3') with 10 base-long length were pared by dissolving into a 0.165M phosphate buffer solution with a pH value of 7.2. The synthetic DNA was purified throuth high performance liquid chromatography resulting in a final pruity above 98%. Fig. 5 shows the channel current varition of poly-Si nanowires with HfO_2 sensing membrane as a function of DNA concentration. The lowest detection limit is about 0.01nM, which is higher than the previou report in Ref. 12 with SiO_2 sensing membrane. The improvement of HfO_2 sensing film is attributed to the enhanced dielectric capacitance, giving rise to the coupling of electrical signals.

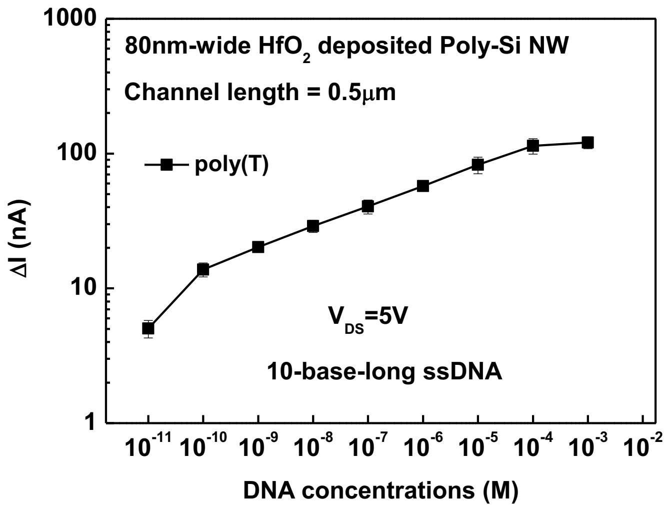


Fig.5 The channel current variation ΔI measured at a drain-source voltage of 5V as a function of DNA concentration.

Conclusions

High performance poly-Si nanowires with high-k sensing membrane for pH sensing and DNA detection are proposed via a simple and low-cost sidewall spacer formation. The sensing characteristics are strongly depended on crystallinity, k-value, and leakage current of dielectric membrane. The experimental results show that the pH sensitivity is increased in the order of HfO_2, TiO_2, and Al_2O_3. The HfO_2 sensing film with best sensitivity can be ascribed to the higher k-value than Al_2O_3 and lower leakage current than TiO_2. Furthermore, the HfO_2 sample exhibits the highest number of assay tests due to the polycrystalline structure. In addition, the proposed poly-Si nanowire sensor can detect a 10-base-long single-strained homopolymers DNA molecule solution with an ultra-low concentration of 0.01nM. Therefore, the poly-Si nanowires with HfO_2 membrane is very promising for the pH sensor and DNA detector applications.

Acknowledgments

This work was supported by the National Science Council of the Republic of China under the Grant Number NSC 99-2221-E-009-168-MY3. Also, the authors would like to thank the Nano Facility Center (NFC) of National Chiao Tung University and the National Nano Device Laboratory (NDL) for facility utilization.

References

1. P. Bergveld, *IEEE Trans. Biomed. Eng.*, **BME-17**(1), 70 (1970).
2. J. C. Chou, C. Y. Weng, and H. M. Tsai, *Sens. Actuators B.*, **81**(2-3), 152 (2002).
3. A. Simonis, C. Ruge, M. Muller-Veggian, H. Luth, and M. J. Schoning, *Sens. Actuators B.*, **91**(1-3), 21 (2003).
4. M. J. Schoning, D. Brinkmann, D. Rolka, C. Demuth, and A. Poghossian, *Sens. Actuators B.*, **111-112**, 423 (2005).
5. J. C. Chou and J. L. Chiang, *Sens. Actuators B.*, **66**(1-3), 106 (2000).
6. C. Y. Wu, T. C. Liao, M. H. Yu, S. K. Chen, C. M. Tsai, and H. C. Cheng, *Microelectronics Reliability*, **50**, 704 (2010).
7. T. C. Liao, S. W. Tu, M. H. Yu, W. K. Lin, C. C. Liu, K. J. Chang, Y. H. Tai, and H. C. Cheng, *IEEE Electron Device Lett.*, **29**, 889 (2008).
8. C. Y. Wu, Y. T. Liu, T. C. Liao, M. H. Yu, and H. C. Cheng, *IEEE Electron Device Lett.*, **32**(8), 1095 (2011).
9. P. Y. Hsu, J. J. Lin, Y. L. Wu, W. C. Hung, and A.G. Cullis, *Sens. Actuators B.*, **142**(1), 273 (2009).
10. C. D. Fung, P. W. Cheung, W. H. Ko, *IEEE Trans. Electron Devices*, **ED33**, 8 (1986)
11. D. Shamiryan, M. Baklanov M. Claes, W. Boullart, and V. Paraschiv, *Chem. Eng. Comm.*, **196**, 1475 (2009).
12. Y. L. Wu, P. Y. Hsu, C. P. Hsu, and W. C. Liu, *J. Electrochem. Soc.*, **157**(6), J191 (2010).