

P11-2 Ion Polarity Dependent Voltage Shifts of SiGe Membrane for pH Sensor

Chao-Sung Lai, Chia-Ming Yang, Chih-Yao Wang and Ti-Chuan Wang

Department of Electronic Engineering, Chang Gung University,
259 Wen-Hwa 1st Road, Kwei-Shan Tao-Yuan 333, Taiwan
Phone: +886-3-2118800 ext. 5786 E-mail: cslai@mail.cgu.edu.tw

1. Introduction

The feasibility on introducing SiGe membrane for hydrogen ions was first proposed in our research [1]. Silicon germanium (SiGe) was applied to enhance hole mobility in pMOSFETs [2] and form nanocrystal in memory devices [3]. Ion Sensitive Field-Effect Transistors (ISFETs) could be fabricated by VLSI technology with the advantages of small size, low cost, high input impedance, low output impedance and rapid response over conventional ion selective electrode [4-5]. In this work, the hydrogen ion sensitivity and ion polarity dependence on SiGe membrane was investigated. Hysteresis loop measurement and a physical model for SiGe membrane was proposed also.

2. Experiment

The pH sensing properties of SiGe membrane were all extracted by capacitance-voltage (C-V) curves of Electrolyte-Insulator-Semiconductor (EIS) structures. The process flows were summarized as shown in Fig. 1. P-type (100) Si wafers were used to grow silicon dioxide to the thickness of 500Å by thermal oxidation at 950°C after standard RCA cleaning. SiGe membranes were deposited by low pressure chemical vapor deposition (LPCVD) at fixed 475°C and 100mtorr. A 10Å thickness amorphous silicon (α -Si) layer was deposited on the thermally grown SiO₂ by pure Si₂H₆ gas. Then, SiGe layer was deposited by Si₂H₆ and GeH₄ mixed ambient for a thickness of 500Å. A photosensitive epoxy, SU8, was used to define sensing area. The EIS structure was schematic in Fig. 2.

SiGe membranes were analyzed by Auger Electron Spectrometer (AES) for the depth profile. C-V curves for various pH buffer solutions of Merck Inc. were measured through Ag/AgCl reference electrode by HP4284A. Avoiding to anodic oxidize on reference electrode, the substrate of EIS structure was biased from 3 to -3V. The pH hysteresis loop measurement protocol was shown in Fig. 3 for (a) base to acid and (b) acid to base, denoted as B-A-run and A-B-run, respectively. For B-A-run, C-V measurements were performed from base (pH10) to acid (pH2) by increasing hydrogen ion concentration. For A-B-run, C-V curves were measured from pH2 to pH10.

3. Results and Discussions

Typical pH response of SiGe EIS

The typical C-V curves of SiGe EIS in B-A-run were shown in Fig. 4. The C-V curves were shift to positive bias as increasing hydrogen ion concentration. Flatband voltages (V_{FB}) in each pH solution of B-A-run were extracted as shown in Fig. 5. The sensitivity can be calculated as equation (1):

$$\text{Sensitivity} = \Delta V_{FB} / \Delta pH \quad (1)$$

The calculated sensitivity of SiGe EIS was 59.77mV/pH and the linearity was 99.84%. This performance of SiGe EIS is comparable to other applied ion sensing material, such as Ta₂O₅ and Al₂O₃ [4].

Polarity dependent voltage shifts in A-B run

The V_{FB} distribution of A-B-run was shown in Fig. 6. Extracted sensitivity is 64.94mV/pH with poor linearity, 97.784%. Comparing to B-A run, the absolute flatband voltages of all measurement variations were shown in Fig. 7. The V_{FB} differences between B-A-run and A-B-run were almost up to 100mV in the hysteresis measurement. These asymmetric behaviors in B-A-run and A-B-run were assumed highly relative to polarity dependence by hydrogen ions.

Ion Polarity dependent mechanism

The compositions of SiGe membrane were verified by AES depth analysis as shown in Fig. 8. Oxygen content near surface could be due to native oxidation of SiGe. This native oxide layer is less resistant to acid buffer solution than other sensing membrane. We proposed an ion polarity dependent mechanism demonstrated particularly in Fig. 9. There was a hydration layer formation in pH10 buffer and keep H⁺ ions from penetrating into SiGe membrane. Ion sensing performance of SiGe with hydration layer was closed to Nernstain response by surface binding sites. When hydration layer was removed in pH2 buffer, then voltage shifts would be dominated by the reaction equilibrium between penetration and out-diffusion rate of extra hydrogen ions in each pH buffer. Therefore the fitted sensitivity would be contributed by two components, one is site binding potential and another one is H⁺ ion polarity dependent induced voltage shifts as listed in equ. (2).

$$V_{bi}' = V_{bi}(\text{site} - \text{binding}) + \Delta V_{bi}(\text{polarity dependent}) \quad (2)$$

The polarity of induced ΔV_{bi} is negative and positive for H⁺ ions penetrating into SiGe and out-diffusing from SiGe, respectively. Based on this mechanism, hydration layer would retard hydrogen ions penetrate into SiGe. Site-binding dominated in both B-A-run and A-B-run. Another pH hysteresis loop measurements between pH 10 and pH6 were performed to verify this assumption. An obvious improvement in ΔV_{bi} of A-B-run is decreased to 5.95mV due to immunity of hydrogen ions penetration by hydration layer.

4. Conclusions

A systematic study on hydrogen ions polarity dependent voltage shifts of SiGe sensing membrane was proposed. The sensitivity of SiGe EIS was 59.44mV/pH. The asymmetric behaviors between B-A and A-B run were explained by our proposed ion polarity dependent model.

Acknowledgement

This work was supported by the National Science Council under the contract of NSC 93-2215-E-182-002.

References

- [1] C.M. Yang, C.S. Lai, et al., Microele. Eng. **80** (2005) 46
- [2] Zhonghai Shi, et al., Appl. Surf. Sci. **224** (2004) 248
- [3] D.W. Kim, et al., IEEE Trans. ED **50** (2003) 1823
- [4] T. Mastsuo, et al., Sens. & Actu. **1** (1981) 77
- [5] J.C. Chou, et al., Jpn. J. Appl. Phys. **41** Part1 (2002) 5941

- Standard RCA clean
- Dry oxidation 500Å
- LPCVD for a-Si 10Å
- LPCVD for SiGe 500Å
- Al backside electrode
- SU8 definition
- PCB attached and Epoxy package

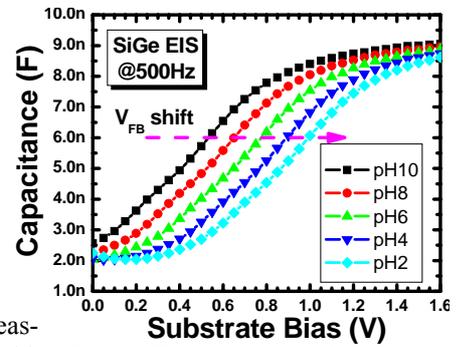
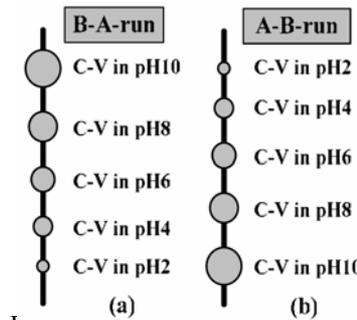
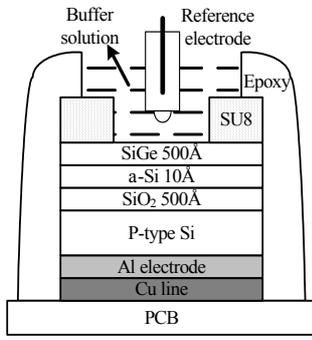


Fig. 1 The process flow of SiGe EIS in this work

Fig. 2 The schematic cross section structure of SiGe EIS including reference electrode.

Fig. 3 The pH hysteresis loop measurement on SiGe EIS for (a) base-to-acid (B-A-run) and (b) acid-to-base (A-B-run), respectively.

Fig. 4 The typical C-V curves of SiGe EIS structure in different pH buffer solution.

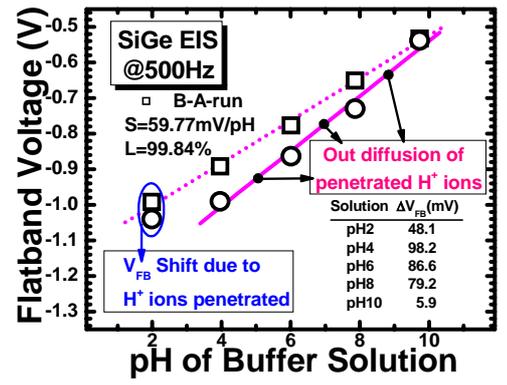
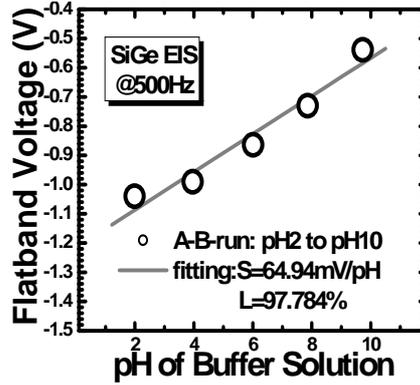
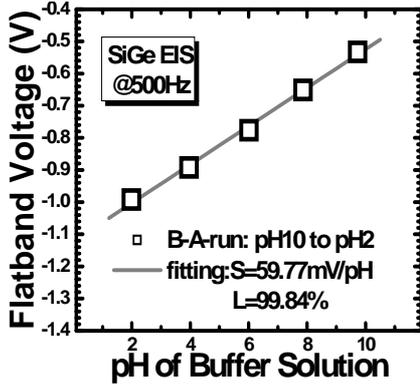


Fig. 5 The extracted flatband voltages of each pH solution in B-A-run. Sensitivity is 59.77mV/pH and the linearity is 99.842%.

Fig. 6 The extracted flatband voltages of each pH solution in A-B-run. The linearity is 97.784%.

Fig. 7 The flatband voltages distribution of whole pH hysteresis loop composed of B-A-run and A-B-run.

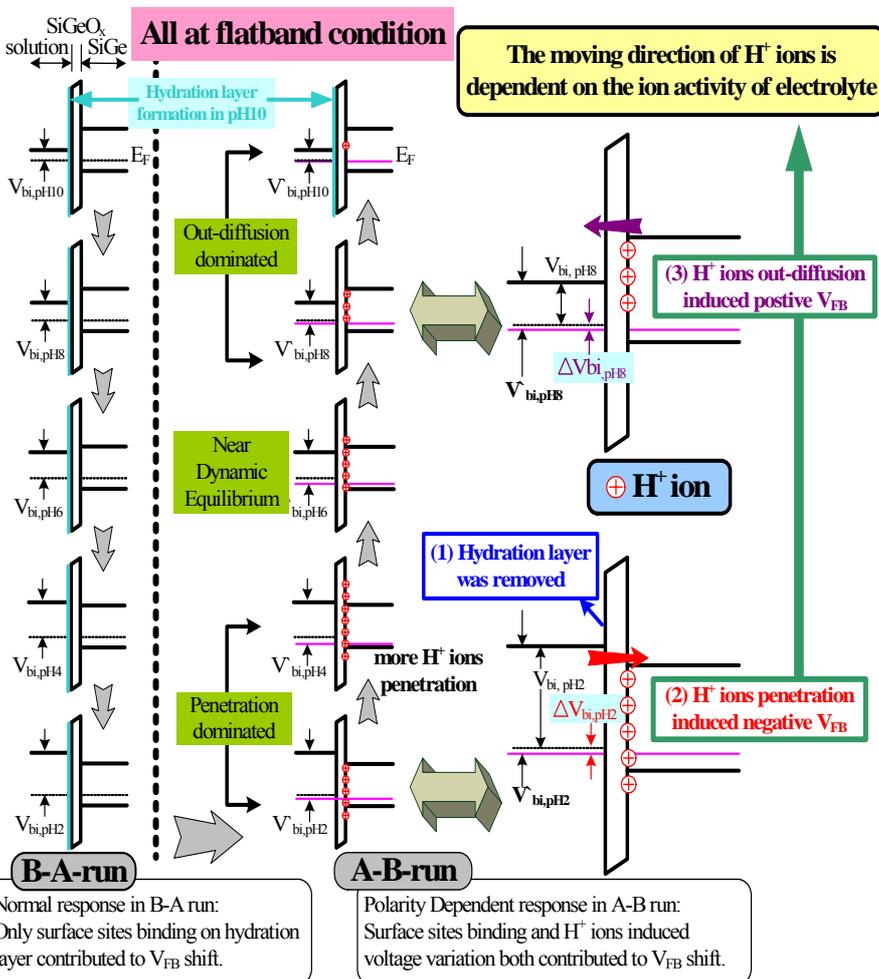


Fig. 9 Our proposed mechanism for the asymmetric behavior in pH hysteresis loop explained by hydrogen ions penetrated into SiGe in acidic solution and then out-diffused in basic solution.

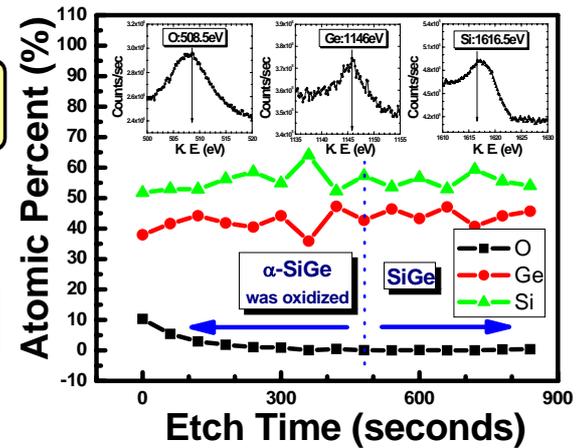


Fig. 8 The compositions of SiGe membrane are Si, Ge and O demonstrated by AES depth analysis.

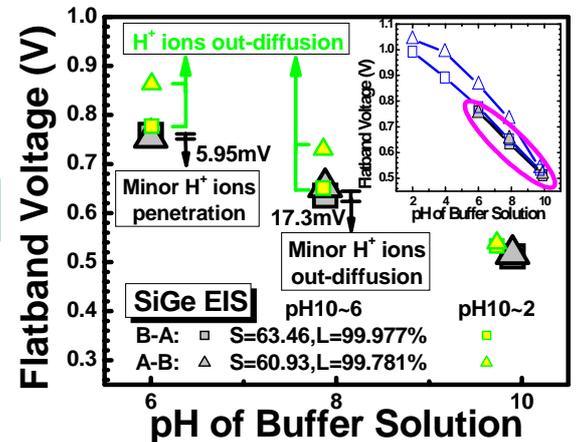


Fig. 10 The flatband voltages distributions of additional pH hysteresis loop measurements with different loop width could be supported by our proposed mechanism.