pH and pK sensing modification by cosputtered TiSiON/SiO₂/Si electrolyte-insulator-semiconductor structure

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Abstract

Cosputtered TiSiON with target power adjustment and rapid thermal anneal (RTA) treatment is firstly investigated pH and pK sensing performance of electrolyte-insulator-semiconductor (EIS) structure. This methodology can be easily applied into standard CMOS and DRAM technology since TiN and SiO₂ are well-verified material. pH sensitivity of 39 mV/pH could be obtained in TiSiON/SiO₂ EIS structure with Si power of 150W and its pK sensitivity could be increased from 9 to 21 mV/pK with RTA at 800°C. Higher surface roughness shown in AFM analysis and higher Si level shown in XPS could be the reasons of increased pK sensitivity.

1. Introduction

SiO₂ is the first sensing material applied in ion-sensitive field-effect transistor (ISFET), which is not good enough for pH sensing since the linear range is not wide and higher interference by other ions including potassium and sodium [1]. TiN is a widely used material for buffer or barrier layer between metal and semiconductor in current VLSI technology, which is proved as a promising pH sensing material as an extended-gate field- effect-transistor (EGFET) [2-3]. To have a multi-ion sensing application, modification of TiSiON sensing membrane by power of Si target in radio frequency sputter and following a RTA treatment at different temperature are presented firstly in this study.

2. Experimental

Double-layer EIS structures were fabricated to investigate H⁺ and K⁺ ion sensing properties of TiSiON. TiSiON was deposited by cosputter with Ti and Si target in radio frequency sputtering directly on p-type (100) silicon wafer after standard RCA cleaning and thermally grown SiO₂ with thickness of 30 nm. The Ti target with 99.95% purity was set with power of 100 W and Si target with 50, 100 and 150W as experimental conditions, respectively. Total flow rate of Ar, O₂ and N₂ kept same. RTA treatments are performed at different temperature as second experimental condition. C-V measurements are performed through reference electrode by HP4284A high precision LCR meter.

3. Results and Discussion

As shown in Fig. 1, C-V curves were measured in various standard pH buffer solutions to collect the pH sensing response of TiSiON/SiO₂ EIS with 50W of Si target sputtering. pH sensitivity of 52 mV/pH can be calculated by the linear fitting between the output voltage and pH value as shown in the inset. Linearity of 99.8% in the fitting curve can be a good index for wide pH range. Detail comparison on pH sensitivity distribution of all 12 experimental groups as shown in Fig. 2. With RTA temperature increases, pH sensitivity could be obviously decreased. To confirm the pH sensing stability, hysteresis measurement of pH loop of pH 7-4-7-10-7 with 3 continuous measurements lasting for 5 min as shown in Fig. 3(a). Very small hysteresis of 1.56mV could be observed in TiSiON/SiO2 EIS with 150W of Si target sputtering and RTA at 800°C as shown in Fig. 3(b). C-V curves measured in pK 0 to pK3 are shown in Fig. 4. pK sensitivity and linearity are calculated as 25.3 mV/pK and 99.2 % as shown in the inset. As shown in Fig. 5, the smallest distribution of flatband voltages is samples with 700°C RTA. With RTA temperature increases, pK sensitivity and linearity could be improved as shown in Fig. 6(a) and (b), respectively. Surface roughness and morphology of AFM analysis decreased with RTA temperature as shown in Fig. 7 (a) to (d), which could be used to explain by site-binding model. [4] Si spectrum of XPS is observed with higher intensity in higher power of Si target, which could lead to different surface composition, types of sites and dissociation coefficient. [5] Therefore pH and pK sensitivity could be adjusted by this difference in surface composition.

4. Conclusions

Different power of Si target was investigated for TiSiON sensing membrane for the first time. Higher power makes lower pH and high pK sensitivity, respectively. 150W at Si target and then with RTA at 700°C is observed as a potential pK sensing performance with sensitivity of 21 mV/pK and linearity of 99.9%. A further pK sensing performance could be suggested to performed CF₄ plasma treatment on this TiSiON sensing membrane. [6]

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References

- [1] P. Bergveld, Sensors and Actu., B: Chemical 88 (1), pp. 1-20
- [2] Y.-L. Chin, et al., Jpn. J. Appl. Phys. 40 (2001) 6311.
- [3] Y. Rayanasukha, et al., Adv. Mat. Res. 802, (2013) 232.
- [4] C.-S. Lai, et al., Electrochem. Solid-State Lett. 9 (2006) G90.
- [5] C.-M. Yang, et al., J. Electrochem. Soc. 155 (2008), J326. [6]
- T.-F. Lu, et al., J. Electrochem. Soc. 158 (4), (2011) J91.



Fig. 1 C-V curves of TiSiON EIS structure with 50W of Si target sputtering without RTA measured in different pH buffer solution and its sensitivity and linearity.



Fig. 2 pH Sensitivity of TiSiON EIS structure with different RTA tempeature and sputter power of SiO_2 target.



Fig. 3 Hysteresis performance of TiSiON EIS with 50W of Si target sputtering and (a) without and (b) with RTA at 800°C measured in the loop of pH7-4-7-10-7.



Fig. 4 C-V curves of TiSiON EIS for pK 3-pK 0 and its sensitivity and linearity.



Fig. 5 Flat-band voltage distribution of TiSiON EIS structure with 150W for Si target sputtering.



Fig. 6 (a) pK sensitivity and (b) linearity of TiSiON EIS structure with 150W for SiO_2 target.



Fig. 7 AFM analysis of TiSiON EIS structure with RTA at (a) without, (b) 600, (c) 700, and (d) 800 °C.



Fig. 8 Si spectrum of XPS in TiSiON layers with different power of SiO2 target.