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Frequency dependences of pH sensitivity and light immunity for single and stacked HfO_2 EIS structures

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1. Introduction

Capacitance to voltage (C-V) measurement is a normal but useful method to know the electrical behavior for metal insulator semiconductor (MIS) capacitor. In 1979, a similar structure, electrolyte-insulator-semiconductor (EIS) was developed as a capacitive sensing platform. [1] To form the EIS structure, the metallic gate electrode is replaced by a reference electrode in electrolyte. The C-V curves of EIS structure are shifted with the variation of ion concentration because of the surface site-binding mechanism. However, the analysis for pH sensitivity and light immunity was dependent on the C-V measurement. So, a suitable frequency of ac signal and equivalent impedance mode should be optimized. However, there is no publication fully demonstrate the relationship between C-V measurement setup and pH sensing properties.

In this work, the frequency dependences of pH sensitivity and light immunity were systematic studied. For comparison the EIS capacitor with HfO_2 (single) and HfO_2/SiO_2 (stacked) sensing membranes were prepared. A novel approach to optimize pH sensitivity and light immunity was proposed. Two equivalent circuits with serious (C_S-R_S) and parallel (C_P-R_P) modes were used to extract the impedance parameters. Some tradeoff among the various factors can be made within the parameter space bounded by illumination effect, ac frequency, structure, and measurement modes. This new design methodology can be applied to optimize the sensing performance.

2. Experiment

The insulator layer of EIS structure (Fig. 1) was formed with single HfO_2 or HfO_2/SiO_2 layer. HfO_2 layer was deposited by radio frequency (rf) reactive sputtering on p-type (100) silicon wafer with or without 50 nm thermally grown silicon dioxide (SiO_2). During the reactive rf sputtering, Hf target with 99.9% purity was used in the ambient of Ar and O_2 with the ratio as 20: 5. The rf power and process pressure is 150 Watt and 20 mTorr, respectively. To have the backside ohmic contact, aluminum layer formed by thermal evaporator was used. Sensing area of EIS structure was opened with fix dimension by photosensitive epoxy SU8. Afterwards, EIS structures were assembled onto the print circuit and coated with epoxy resin manually. [2]

All C-V curves of EIS structures were measured by high-precision LCR meter, HP 4284A. As shown in Fig. 2, the frequencies of AC signal were set from 100 to 500 kHz with the C_P-R_P and C_S-R_S modes, respectively. The pH sensitivities were calculated from the corresponding voltage at $0.6C_{MAX}$ in the buffer solution of pH 4, 7, 10. [3] Considering the light effect on voltage shift and pH sensitivity, the measurement setup was shielded in a dark box or opened to normal indoor light illumination. [4, 5]

3. Results and discussion

I. Basic C-V characteristics

At first, the frequency dependence of the measured C-V curves for single and stacked EIS structures with C_P-R_P or C_S-R_S mode in dark and illumination were shown in Fig. 3, respectively. Noise disturbance was only shown in the C-V curves measured at 100Hz. Stacked EIS structure showed the higher sensitive to illumination than single EIS structure due to capacitance increasing more in inversion mode. And C_S-R_S mode enhanced this behavior more than C_P-R_P mode. In Fig. 4, the frequency dispersion was serious in the C_{MAX} variation for single structure than stacked one, especially for C_P-R_P mode.

II. The sensitivity to hydrogen ion concentration

Pure pH sensing response of EIS structure can be measured in dark box. The distribution of pH sensitivity and corresponding linearity were shown in Fig. 5. The pH sensitivities for both structures showed almost the same response with different frequencies and C-R modes. The pH sensitivity for single structure is 58-60 mV/pH, which is obviously higher than the stacked structure (44-48 mV/pH). The sensitivity for higher frequency can not be obtained because the C_{MIN} higher than $0.6C_{MAX}$ as shown in Fig. 6.

III. Voltage shift and pH sensitivity in illumination

Light effect on EIS structure was measured in the indoor illumination environment. In Fig. 7, the corresponding voltage of 0.6 C_{MAX} at pH 4 shifted with different frequency in illumination. The voltage shift caused by illumination is smaller for single EIS structure than stacked one. Light effect for EIS structure could be minimized at suitable frequency range and equivalent impedance mode. The pH sensitivities for single and stacked EIS structure measured in illumination were shown in Fig. 8. Finally, the suitable range of frequency with C_S-R_S and C_P-R_P mode for pH sensing properties and light effect were summarized in Table I.

4. Conclusions

In this study, pH sensitivities are almost no influence by ac frequency and C_S-R_S and C_P-R_R mode, but light induced drift can be minimized by using a suitable range of frequency. The single EIS structure showed better performance with higher pH sensitivity as 57 mV/pH, and light induced drift can be minimized to around -15 mV with frequency of 100 to 1k Hz in C_P-R_P mode. It can be applied in illumination with the pH sensitivity as 54-58 mV/pH.

Acknowledge

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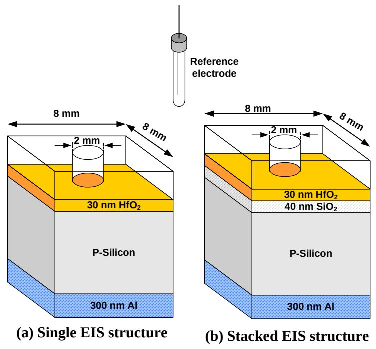

Fig. 1 (a) Single and (b) stacked capacitive EIS structure.

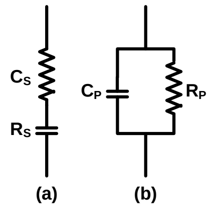

Fig. 2 The equivalent circuit of (a) C_S-R_S model and C_P-R_P model in C-V measurement

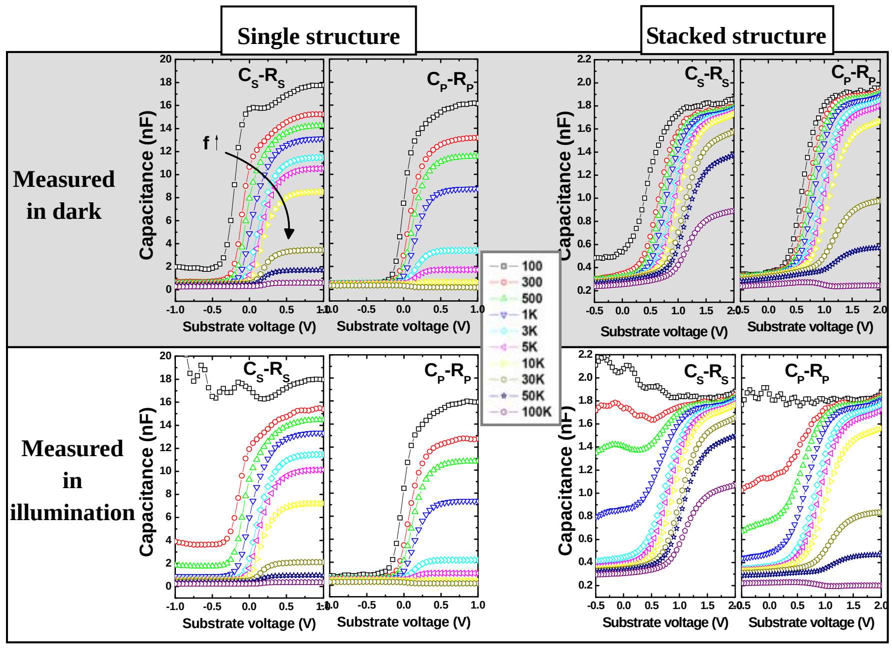

Fig. 3 The C-V curve for single and stacked EIS structure with different frequency of ac signal based on C_S-R_S or C_P-R_P mode in dark and illumination

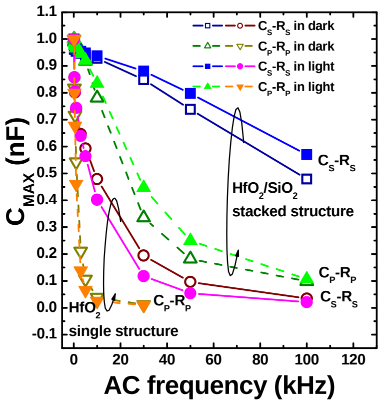

Fig. 4 The normalized C-F curve for single and stacked EIS structure with C_S-R_S and C_P-R_P mode in dark and illumination, respectively

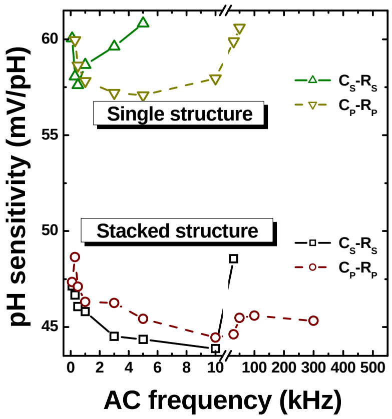

Fig. 5 The distribution of pH sensitivity and corresponding linearity for single and stacked structure with different measurement mode (C_S-R_S & C_P-R_P) and frequency of ac signal

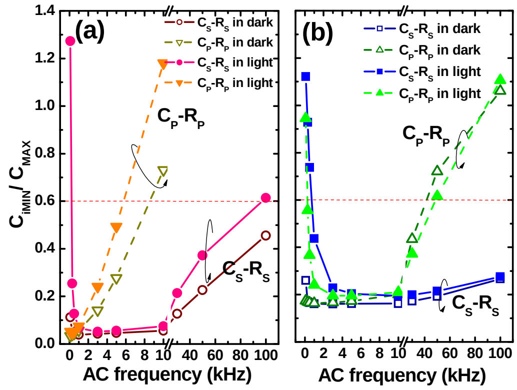

Fig. 6 To determine the corresponding VG of 0.6 C_{MAX} is existed or not, the ratio for C_{MIN}/C_{MAX} of (a) single and (b) stacked EIS with C_P-R_P and C_S-R_S mode were shown, respectively.

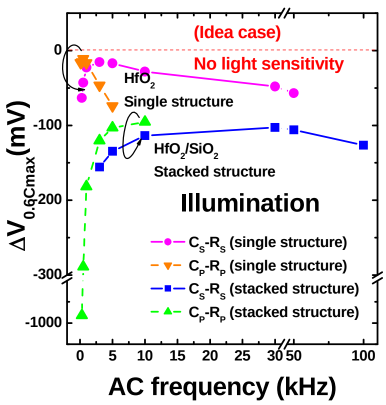

Fig. 7 The corresponding voltage shift of single and stacked EIS structure at different frequency with C_S-R_S or C_P-R_P mode, respectively

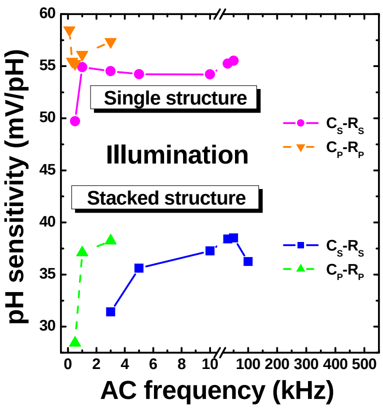

Fig. 8 The distribution of pH sensitivity and linearity for both structure with C_S-R_S and C_P-R_P and frequency of ac signal in indoor light illumination

Table I The suitable range of frequency and C-R mode for pH sensing properties and light effect on both structure, respectively.

Struc.	C-R mode	In dark: Sens. (mV/pH)	In dark: Suitable freq. (Hz)	In illuminative condition: Optimal Vg shift (mV)	In illuminative condition: Suitable freq. (Hz)	In illuminative condition: Sens. (mV/pH)
HfO_2	C_S-R_S	57-60	100-100k	-15~-17	1k-5k	54
	C_P-R_P	57-63	100-5k	-11~-16	100-1k	55-58
HfO_2/ SiO_2	C_S-R_S	45-47	100-300k	-102~-105	3k~5k	36-37
	C_P-R_P	44-46	100-10k	-95~-103	5k~10k	36-38.5