Low temperature Ta₂O₅/X-doped Al₂O₃/SiO₂/Si for pH sensing membrane by spray pyrolysis doped system

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Abstract

A X-doped Al_2O_3 layer with negative charge was proposed as a embedded layer in EIS structure for better pH sensing properties. The EIS with heavy doped Al_2O_3 layer which sensing properties including sensitivity, hysteresis and drift are 57.4 mV/pH, 1.14 mV and,0.138 mV/h respectively.

1. Introduction

The concentration of hydrogen (H⁺) ion is one of the most important index for environment monitoring and disease prevention. Many kinds of sensor have been applied in ion examination, including ion sensitive field-effect transistor (ISFETs), light addressable potentiometric sensor (LAPS) and ion-selective electrodes (ISEs). Among of proposed sensor, ISFET is an attractive platform for pH detection [1-3].

In this work, a new stacked X-doped Al_2O_3 layers deposited on SiO₂/Si wafer with Ta₂O₅ sensing membrane by spray pyrolysis deposition (SPD) was demonstrated. SPD is a simple technique with advantages including low-cost, low-temperature (300°C), large area, easy doping and charges embedded. A novel X-doped Al_2O_3 thin films have been deposited by SPD with negative charged embedded to attract positive hydrogen ions and improve the sensing characterization including sensitivity, hysteresis and drift phenomenon.

2. Experiment

A standard EIS structure with triple oxide layers was chosen for the sensing platform. The schematic structure and the fabrication process flow were shown in Fig. 1(a). X-doped Al_2O_3 layer were deposited on SiO₂ with various X-dopant concentration by spray pyrolysis deposition (SPD) system. To form the sensing membrane, Ta_2O_5 layer was deposited by rf. reactive sputtering with a Ta target. Afterwards, aluminum layer formed by thermal evaporator was used for the backside contact. The sensing area was defined by photolithography with SU-8 photo resist. Finally, the EIS structure were packaged onto the print circuit board by silver gel and coated by JU-100 epoxy to prevent the leakage fromm the electrolyte.

Capacitance-voltage (C-V) curves of EIS structures measured in various pH buffer solutions were performed by

HP4284A through Ag/AgCl reference electrode. EIS samples were immersed in reversed osmosis water for 12 h to have stable surface status. To investigate the stability of EIS samples, long-term measurement was performed in pH 7 buffer solution. The hysteresis behavior of EIS structure was measured in the pH loop as pH $7 \rightarrow 10 \rightarrow 7 \rightarrow 4 \rightarrow 7$.

3. Results and discussion

Fig. 2 shows the C-V curves of EIS structure measured in various pH buffer solutions. The corresponding pH sensitivity was depicted in the inner figure. pH sensitivity distribution of EIS structures with different X dopant concentration in Al₂O₃ layer was shown in Fig. 3. The highest sensitivity, 57.4 mV/pH, was found in the sample with heavy X doping of Al₂O₃ layer. Because of higher negative fixed oxide charge from high X dopant concentration of Al₂O₃ layer, more hydrogen ion close to the sensing surface by attractive force results in higher pH sensitivity [4]. Fig. 4 shows the hysteresis width of gate dielectric with various concentration of X dopant. The hysteresis widths in pH 7 buffer solution are 1.14 mV, 2.02 mV and 2.95 mV for heavy doping, normal doping and undoping, respectively. The non-ideal effect of hysteresis widths were decreased with doping concentration increases. Fig 5 shows the long-term output voltage of EIS structures measured in pH 7 buffer solutions for 12 h and the drift rates were calculated by linear fitting from 5 h to 12h. The best long-term stability as lowest drift rate, 0.138 mV/h, is observed in samples of heavy doping Al₂O₃ layer. The sensing properties of EIS structures with various X dopant concentration of Al₂O₃ layer are summarized in Table I.

4. Conclusion

In this study, the improvement of sensing properties was demonstrated by the inset of Al_2O_3 layer with heavy doping of X material which could be a candidate for real pH sensor application.

5. Reference

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Figure 1: The schematic EIS structures and fabrication process flow (b)System of spray pyrolysis deposition



Figure 2: C-V curves with the EIS structure immerse into different pH value of buffer solutions



Figure 3: The distribution of pH sensitivity for EIS structure with various metal concentration of X-doped Al_2O_3 layer



Figure 4: Hysteresis widths of EIS structures during the pH=7 \rightarrow \rightarrow 7 \rightarrow 4 \rightarrow 7 loop.



Figure 5: The drift rates of EIS structure in pH 7 buffer solution for 12 hr

Table I :Sensing properties of EIS structure for various concentration of X-dopant in Al_2O_3

| Doping | Sensitivity (mV/pH) | Hysteresis (mV) | Drift (mV/hr) |
|----------|------------------------|--------------------|------------------|
| Heavy | 57.4 | 1.14 | 0.138 |
| Normal | 54.4 | 2.02 | 0.376 |
| Undoping | 51.4 | 2.95 | 1.358 |