# ELECTROLYTE-OXIDE-SEMICONDUCTOR STRUCTURES AS PH SENSORS BASED ON RESISTIVE-SWITCHING CHARACTERISTIC

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## ABSTRACT

An electrolyte-oxide-semiconductor (EOS) structure is reported as a pH sensor in this paper, which provides a new method of pH sensing based on the resistive-switching characteristic for the first time. The concept of conductive filaments is introduced for EOS structures to explain their resistive-switching property. We find that the threshold-voltage shift in the C-V and I-V curves approximately linearly increases with the augment of electrolyte solution's pH value from 1 to 12, showing a linear sensitivity about 46.3 mV/pH. The easily fabricated EOS sensor array could provide multiple and synchronic measurements. The different reverse leakage-current phenomena of EOS sensors with different electrolytes might broaden chemical sensing applications.

## INTRODUCTION

With the development of industry, there are some seriously bad influence on the nature environment like water pollution and accompanying problems such as food safety. For the past decade, various intelligent devices are widely used, which increases the demand of mobile bio-detection and chemical analysis. However, traditional experiments of biosensing and chemical characterization need lab rooms and large machines which costs a lot and also makes the test difficult for mobile application and rapid detection [1].

Recently micro-electro-mechanical system (MEMS) has drawn more and more attention as an applicable method because of its great biocompatibility, lowcost and integrated-circuit (IC) compatible fabrication process. As an important branch of MEMS study, micro/nano-fluidic analytical system plays a critical part in biological and chemical research. Several studys has reported that the electrolyte-insulator-semiconductor field-effect transistor (EISFET) is a promising candidate device for biosensing and chemical analysis in micro/nano-fluidics [2, 3]. The EISFET structure is similar to the MOSFET structure consisting of the source, drain and body contacts. The difference is that there are an electrolytic solution and a reference electrode instead of a gate contact in the EISFET [1]. One of the commonly used specific EIS structure is electrolyte-oxide-semiconductor (EOS) structure. The chemical sensing application of EOS such as pH response in electrolytic solution has been studied by Diot et al. [4]. However, the $SiO_2$/Si interface state density is mainly considered at that time. Further development is limited due to the electrical breakdown and leakage current problems.

Here, our work shows that the oxide layers of EOS structures exhibit resistive-switching characteristic, just like the behavior of dielectric layers in resistive random access memories (RRAMs) [2], when certain voltage is applied between the electrolyte and semiconductor layers. The concept of conductive filaments is introduced for EOS structures to explain their resistive-switching property. The variation of pH value in the electrolytic solution can affect the formation of the conductive filaments, and further affect the resistance characteristic. We utilize this electrical characteristic to achieve pH sensing, which is different from the sensing principle of traditional pH sensors [5].

## FABRICATION AND MEASUREMENT

The EOS sensor is made up of electrolyte trough, $SiO_2$ layer, and heavily-doped Si substrate. The fabrication process is depicted in Figure 1. Phosphorus atoms are diffused into Si substrates to produce n-type doping as shown in Figure 1(a), and phosphorus ion are implanted into the backsides of the substrates, followed by a annealing at 1000 °C for 10 seconds to make the backsides heavily n-type doped. By employing three different processes respectively including low pressure chemical vapor deposition (LPCVD), plasma-enhanced chemical vapor deposition (PECVD), or thermal oxidation, $SiO_2$ layers of different thicknesses are subsequently fabricated on the front sides of the substrates, as shown in Figure 1(b). Then 500 nm Al layers are sputtered on the backsides of the substrates as electrodes where ohmic-contact is required in Al and Si interface as shown in Figure 1(c). Afterwards, in Figure 1(d), the polydimethylsiloxane (PDMS) with an array of circular holes are then bonded together with the $SiO_2$-covered substrate. Without sophisticated structure fabrication processes, a complete EOS sensor is obtained after filling the PDMS reservoirs with electrolytes finally as shown in Figure 1(e).

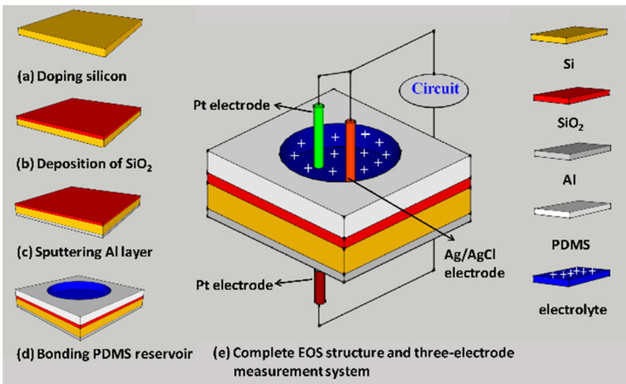


*Figure 1: Schematic of EOS structure, fabrication process and three-electrode measurement system.*

Figure 1(e) also shows a three-electrode method for measuring the electrochemical characteristic of EOS structure. To investigate electrical signals more precisely, two Pt probes are employed as the working electrode and the counter electrode respectively. The counter electrode is contacted with the Al layers, while an Ag/AgCl reference electrode and the working electrode are dipped into the electrolyte solutions. The photo picture of fabricated EOS-sensor arrays and three-electrode measurement setup is illustrated by Figure 2(a). An electrochemical workstation of Gamry Reference 600 (Gamry Instrument, Inc.) is utilized to study the electrical characteristics of the EOS structures. In this paper we mainly test the Current-Voltage (I-V) characteristic and some other characteristics of EOS structures in different conditions to verify the feasibility and validity of EOS-based pH sensors.

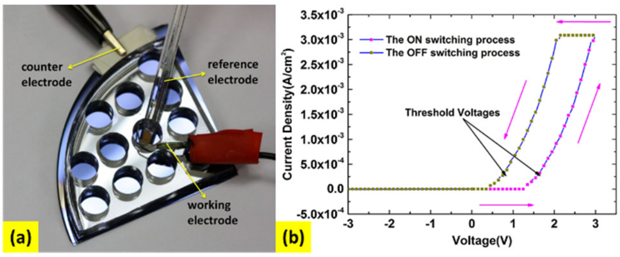


*Figure 2: (a) Photo picture of EOS-sensors; (b) Resistive-switching characteristic of EOS-sensors, taking KCl solution as the electrolyte part.*

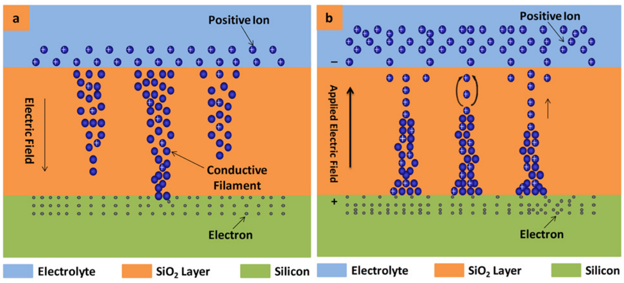


*Figure 3: Schematic (a) formation and (b) dissolution of the conductive filaments in $SiO_2$ layer of EOS structure.*

## RESISTIVE-SWITCHING PROPERTY

A typical I-V curve of one of the EOS sensors is shown in Figure 2(b). An obvious switching window emerges in the I-V curve while the voltage increase from 0 to 3V and then falls back to 0, implying resistive-switching characteristic of the EOS structure. Since $SiO_2$ has already manifested a certain ion conductivity in the study of RRAM, Ir/$SiO_2$/Cu resistance-changing-memory cells for instance [6], and the formation and dissolution of Cu filaments in $SiO_2$ layer are gradually observed as a possible physical mechanism to explain the resistive-switching of RRAM device [7], we developed a hopeful model based on the principle of conductive filament to account for the resistive-switching mechanism of EOS sensors [8]. When the electrolytic solution contacts the $SiO_2$ layer just like the situation in the EOS sensors, there will form an electric double layer at the interface, resulting in the aggregation of movable positive ions at the interface. Those ions can diffuse into the $SiO_2$ layer gradually.

Figure 3 explains what happened in the $SiO_2$ layer schematically. Under a forward bias (the electric potential of electrolyte higher than that of semiconductor), the EOS sensors will turn into a low resistive state (ON switching) because metal ions inject from electrolytic solutions into $SiO_2$ layers because of the applied-electric-field-induced drifting and concentration gradient, forming conductive filaments there, as shown in Figure 3(a). On the contrary, in Figure 3(b), when a reverse bias is applied, positive ions are pull out of the $SiO_2$ layer due to the force of reverse electric field, causing the dissolution of the conductive filaments, which change the EOS sensors to a high resistive state (OFF-switching). In Figure 2(b) we can see that there exist threshold voltages during the two switching processes. These threshold voltages play an important role for the pH sensing based on EOS sensors, which we will discuss later.

## PH SENSING MECHANISM

As described before, for EOS sensors, the switching threshold voltage in the I-V characteristic is mostly concerned in our research. The ON switching threshold voltages will become smaller when the pH values of electrolytic solutions are smaller.

It is supposed that the variation of pH values of electrolytic solutions has great influence on the formation of conductive filaments in the $SiO_2$ layer. Figure 4 is schematic illustration of the pH sensing mechanism. The surface of the $SiO_2$ layer contains –OH functionalities (hydroxyl groups), which are in electrochemical equilibrium with ions in the solutions ($H^+$ and $OH^-$) [9]. Because the hydroxyl groups at the $SiO_2$ surface can be protonated and deprotonated as shown in Figure 4(b), the $SiO_2$ surface potential will change with the pH value when the surface contacts an aqueous solution. When electrolyte solution is acidic or alkaline, $SiO_2$ surface will become positively charged or negatively charged as shown in Figure 4(c) and (d), which leads to increase or decrease of electric field in $SiO_2$ layer. Besides, $H^+$ ions can penetrate into $SiO_2$ layer during the ON switching process and move freely via a hopping process [10]. The mobile $H^+$ ions will also enhance electric field in the oxide layer by Poisson effect. The increase or decrease of electric field in $SiO_2$ layer will make the formation of conductive filaments become easier or more difficult, thus resulting in decrease or increase of the equivalent resistance.

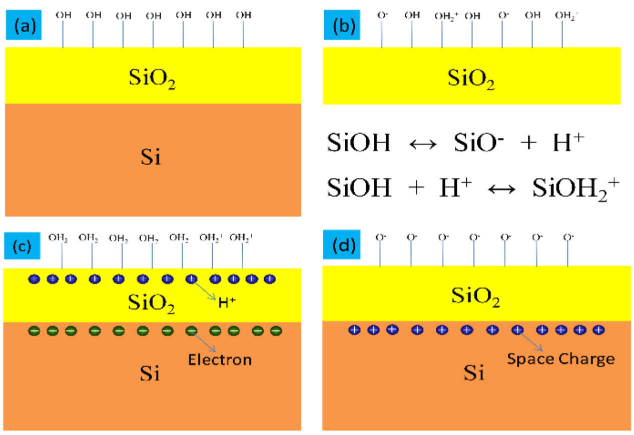


*Figure 4: Schematic mechanism of pH value's effect on equivalent resistance of $SiO_2$ layers in EOS-sensors.*

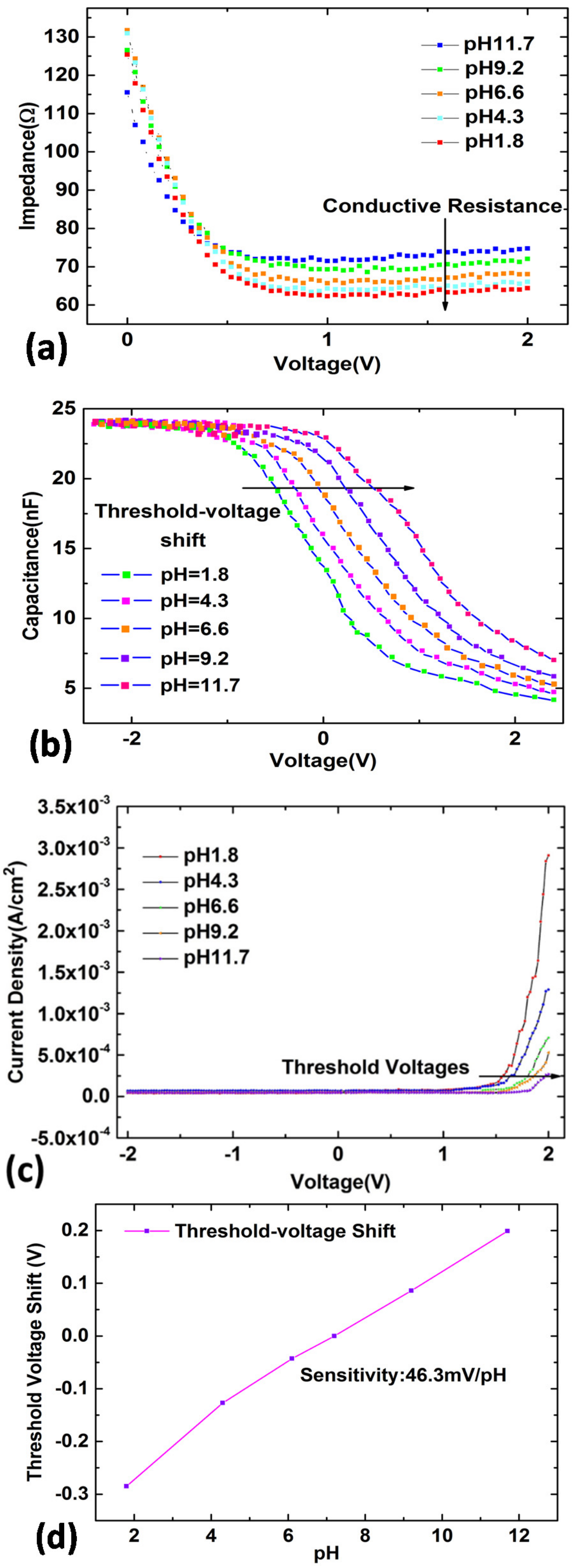


*Figure 5: (a) Impedance-Voltage, (b) Capacitance-Voltage and (c) Current-Voltage responses of the EOS-sensors with different pH values of electrolyte solutions; (d) The relationship between the threshold-voltage shift of EOS-sensors and pH values of electrolyte solutions. It is approximately linear and the sensitivity is about 46.3 mV/pH.*

## EXPERIMENTAL SENSING RESULTS

We test Impedance-Voltage responses of the fabricated EOS-sensors mentioned shown in Figure 2(a) by utilizing KCl solutions with five different pH values from 1.8 to 11.7. The ON switching resistance decreases as the pH value becomes smaller as shown in Figure 5(a). Capacitance-Voltage and Current-Voltage responses of the EOS sensors are also investigated to verify the relationship between the threshold voltage and the pH value. Figure 5(b) indicates that the threshold voltage in the C-V characteristic also increases with increasing of pH value. When focusing on the I-V characteristic in Figure 5(c) and separating the relationship between these two parameters in Figure 5(d), we find that the shift of the threshold voltage almost linearly increases with the pH value. The sensitivity is about 46.3mV/pH, which allows us to measure pH values of electrolyte solutions with the EOS-sensors.

Furthermore, while we test the I-V characteristic of the EOS sensors with different electrolytic solutions containing different metal ions, different leakage-current phenomena arise for these different electrolytes during the OFF switching process of EOS sensors as shown in Figure 6. These interesting phenomena may imply that the unique leakage current for different kinds of electrolytes have potential application in detection of metal ions. That can be a good research direction for the EOS study in future.

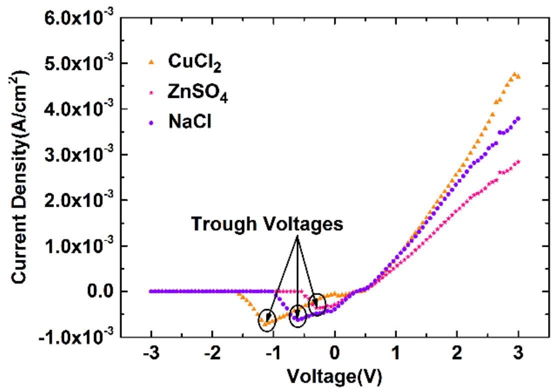


*Figure 6: The reverse leakage-current of EOS structures utilizing $CuCl_2$, $ZnSO_4$ and NaCl solutions. Different electrolytes with different metal ions cause different leakage-current phenomena.*

## CONCLUSIONS

In summary, this paper reports an EOS structure as a pH sensor, providing a new method of pH sensing based on the resistive-switching. The model of conductive filaments is developed to help understand the mechanism of the resistive switching and realization of the pH sensing. The ultimate EOS-sensors can detect pH values of electrolyte solutions from 1 to 12, and have a linear sensitivity of about 46.3 mV/pH. The EOS structures may also be utilized in micro/nano-fluidic systems for ion detection and current control based on the threshold-voltage or reverse-leakage-current of the I-V characteristic. The conductive filament operation model that we propose to understand the resistive-switching characteristic of the EOS structures could also be instructive to further studies and other chemical or biochemical applications.

## ACKNOWLEDGEMENTS

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