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Hybrid anion and cation ion sensors with samarium oxide sensing membrane treated by nitrogen plasma immersion ion implantation

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ABSTRACT

For hybrid anion and cation ion sensing, an electrolyte–insulator–semiconductor (EIS) device with a samarium oxide (Sm_2O_3) sensing membrane treated by nitrogen plasma immersion ion implantation (PIII) was proposed. The N^+ and N_2^+ ions were implanted into the Sm_2O_3 membranes to form the positive charges of N—O and N—O—N bonds, which were investigated by the X-ray photoelectron spectroscopy (XPS). The observed positive charges were then correlated with the resulting anion and cation ion sensing performances. The EIS device with the pure Sm_2O_3 membrane exhibited the mean potassium and calcium ion sensitivity of 36.71 mV/pK and 21.27 mV/pCa respectively because of the main surface sites of O^- groups generated under the pH 8.0 Tris/HCl buffer solution. A high chloride ion sensitivity of 47.92 mV/pCl was obtained from the EIS device with nitrogen PIII treated Sm_2O_3 membrane. This result is attributed to the reaction of OH_2^+ group surface sites with chloride ions by the plasma induced positive charges within the membrane. The drift rate of less than 2.22 mV/h for the Sm_2O_3-EIS device was achieved and suitable for future biosensing use.

1. Introduction

In human body, ions are very important to the human health through their assistance in maintaining homeostasis. For cations, potassium (K^+) and sodium ions (Na^+) act as power generators inside the cells of human bodies [1]. Neurons are cells located throughout the nervous system and communicate information to perform important tasks such as regulating the body temperature or flexing muscles. Calcium ions (Ca^{2+}) play an important role in signal transduction pathways, where it acts as a second messenger [2]. Approximately 99% of the body's calcium is stored in the bones and teeth. For anions, chloride ions (Cl^-) are important in joining with hydrogen ions to make HCl in stomach acid [3]. Chloride and bicarbonate ions (HCO_3^-) are used to maintain the blood's pH level. Different concentrations of Cl^- are either aide or hinder the passing of signals from one nerve cell to another [4]. In 1970, Bergveld proposed the ion-sensitive field-effect-transistor (ISFET), the solid-state electronic device, for chemical sensing of ion concentrations in solution [5]. Caras and Janatas achieved the pioneer work on penicillin detection by the ISFET-based sensing scheme in 1980 [6]. Although the ISFET-based sensors present the advantages of compact size, low cost, rapid response, and ease of fabrication, the electrolyte– insulator–semiconductor (EIS) device, which is the basic structural element of the ISFET, has attracted lots of attention for biomedical, industrial, and environmental applications [7]. The shift of capacitance–voltage (C–V) curves of the EIS devices can be measured according to the changes in surface potential between the electrolyte and sensing insulator.

To develop specific ion sensors, much attention has been paid to the research and development of new sensing materials, commonly known as the sensing membranes, with a good sensitivity and selectivity. It is reported that the high dielectric constant (high-k) samarium oxide (Sm_2O_3) sensing membrane can be used for the superior pH sensing and applied into the urea biosensing [8,9]. The sensing behaviors of the Sm_2O_3 sensing layer on other ions have not been discussed yet. Recently, there are lots of studied dealt with the cation and anion ion sensing layers of the EIS devices. Aluminosilicate glasses or ion implanted silica insulator [10,11], and polyvinyl chloride (PVC) [12] are employed to detect the

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potassium and calcium ions. For example, the potassium ion-implanted sensing membrane, which is compatible with integrated circuit (IC) technology, showed long lifetime but limited K^+ sensitivity [11]. For the researches of anion selective carriers, it is very tedious and laborious [13,14]. Gallium nitride (GaN) (0 0 0 1) grown on sapphire has been used as a sensor element for chloride ions, which presents linear response and is close to the theoretical slope [15]. Perdikaki et al. proposed that multidentate organotin compounds are very attractive molecules for the sensing of chloride ions [16]. Thus, we can find that the polymeric membranes for cation and anion ion sensing present good sensitivity but a short lifetime which is due to the solubilization of the ionophore in the solution and to poor adhesion to the FET device. The inorganic membranes exhibit either limited sensitivity or expensive manufacturing. Up to now, there is no material, which can be used as the sensing membrane both for cation and anion ion sensing. In this work, hybrid anion and cation ion sensors by using the high-*k* Sm_2O_3 sensing membrane with and without nitrogen plasma immersion ion implantation (PIII) treatment respectively have been fabricated. The EIS device with Sm_2O_3 membrane presented mean potassium and calcium ion sensitivity of 36.71 mV/pK and 21.27 mV/pCa respectively because of the formation of O^- group surface sites under the base buffer solution. With the nitrogen plasma immersion ion implantation (PIII) treatment on the Sm_2O_3 layer, the devices showed a chloride ion sensitivity up to 47.92 mV/pCl, depending on the implantation pulse bias, which is attributed to the generation of positive charges of N—O and N—O—N bonds within the Sm_2O_3 membrane. Superior drift properties of the Sm_2O_3-EIS sensors can be obtained for less than 2.22 mV/h.

2. Experimental

2.1. Fabrication of hybrid Sm_2O_3 EIS sensors

The electrolyte–insulator–semiconductor with a high-*k* Sm_2O_3 sensing membrane was fabricated on a 4-in. p-type (1 0 0) silicon wafer with a resistivity of 1–10 Ω-cm. After a standard RCA clean was carried out, a 50-nm-thick SiO_2 layer was thermally grown in a horizontal furnace. Then, all samples were subjected to a sputtered chamber, which has an 8-in.-radius and 15-in.-height cylinder shape, and the throw distance between the targets and substrate was 3 in. Prior to the deposition, the background of the system was pumped down to 10^{-5} Torr, and 3-in.-diameter target of Sm was pre-cleaned by argon plasma for 5 min to remove the native oxides on the surface. Subsequently, a 10-nm-thick Sm_2O_3 layer was deposited by the reactive radio frequency (RF) sputtering system in an ambient containing a mixture of argon and oxygen gases at a pressure of 20 mTorr with Sm (99.9% pure) target. After that, the nitrogen plasma immersion ion implantation treatment was performed at the RF power of 350 W to introduce the nitrogen elements with high dosage into the Sm_2O_3 films. PIII is the new technique that is considered as probable candidate for ion implantation in low energy and high dose region [17]. The implantation was done by applying biasing pulses of 1, 3, and 5 kV amplitude and 10 us duration at 200 Hz frequency for 3 min, denoted as 1 kV, 3 kV, and 5 kV respectively. The sample without treatment was denoted as w/o. All samples were subjected to rapid thermal annealing (RTA) at 700 °C for 30 s in nitrogen ambient. A 300-nm-thick Al film was deposited by using a thermal coater as the backside contact of wafer after removing native oxide using the buffered oxide etchant (BOE) solution. Finally, the negative-photoresist SU8-2005 (MicroChem Inc., USA) was used to define the sensing area, which is a 1-mm-radius circular region, as the electrolyte contact using lithography processing. The above prepared EIS structures were cut and assembled on the copper line of a printed circuit board (PCB) by means of silver gel to form conductive line. A hand-made epoxy package was performed to encapsulate the EIS structure from the copper line. The schematic structure of our hybrid EIS sensors with Sm_2O_3 sensing membrane and nitrogen PIII treatment was displayed in Fig. 1.

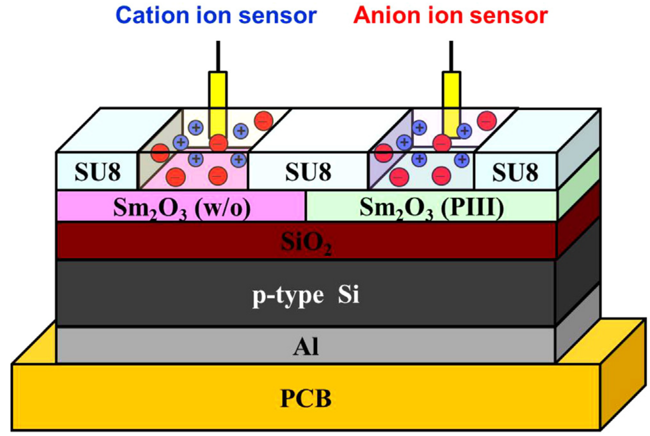

Fig. 1. Device structure of the hybrid anion and cation ion Sm_2O_3-EIS sensors with and without nitrogen PIII treatment respectively.

2.2. Material analysis and pK, pCa and pCl sensing measurements

After the EIS devices have been fabricated, the effect of nitrogen PIII treatment on Sm_2O_3 sensing membrane was investigated using X-ray photoelectron spectroscopy (XPS). On the other hand, to evaluate the resulting EIS-based pK, pCa and pCl sensing performance of the above Sm_2O_3 membranes, a 5-mM Tris/HCl buffer solution of pH 8.0 was prepared. The concentration of K^+/Cl^- and Ca^{2+}/Cl^- ions and in a range between 10^{-4} and 1 M was varied by adding 1 M KCl/Tris–HCl and $CaCl_2$/Tris–HCl standards. The measurement range is suitable for the use in extracellular fluids (ECF) such as serum, where pK is 2.3–2.46, pCa is 2.58–2.62, and pCl is 0.96–1.02 [18]. Briefly, to saturate the ionic properties of the tested sensing membranes, all EIS devices fabricated were firstly immersed in 0.5-mM Tris/HCl for 12 h prior to the measurements [19]. The capacitance–voltage (*C*–*V*) curves for the solutions with varied pK, pCa and pCl levels were then measured through Ag/AgCl reference electrode by Hewlett-Packard (HP) 4284A LCR meter with an ac signal frequency of 100 Hz to keep the equilibrium of the electrochemical system. To reduce the light influence and high frequency noise, all measurement were carried out in a Faraday cage at room temperature (~25 °C). The detection sensitivity of the Sm_2O_3 sensing membranes investigated in this research was then evaluated by the voltage at 60% of maximum capacitance ($0.6 \times C_{max}$) in the linear region of measured *C*–*V* curves [20]. Finally, the drift coefficient was calculated by the linear fitting of the output signal in time range from 4 to 12 h [21].

3. Results and discussion

3.1. Material analysis

Fig. 2(a) displays the STRIM simulation of implantation profile for nitrogen ions embedded in the sensing structure for the biasing pulse of 1 to 5 kV. The secondary ion mass spectrometry (SIMS) profile was well fitted by the STRIM simulation [22,23]. We use the multi-species plasma of N^+ and $N_2{}^+$ for the simulation by tuning the ratio of atomic ions to molecular ions concentrations and single charged atomic ions percentage [24]. The charged particles of molecular $N_2{}^+$ ions are in the prevailing majority and the N^+ and $N_2{}^+$ ions ratio for simulation was approximately 1:8. This is