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Light-Addressable Potentiometric Sensor Treated by Nitrogen Plasma Immersion Ion Implantation for Chloride Ions Detection

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Abstract

In this paper, we demonstrated the light-addressable potentiometric sensor (LAPS) with samarium oxide (Sm_2O_3) membrane treated by nitrogen plasma immersion ion implantation (PIII) for chloride ion sensing. With nitrogen PIII treatment, the sensing behavior of the Sm_2O_3-LAPS device changed from potassium to chloride ions. The optimized chloride ion sensitivity was approximately 35.39 mV/pCl. The device was the first chloride ion sensor with inorganic membrane. Significant sensitivity change as a function of potassium and chloride ion concentration for the nitrogenized Sm_2O_3-LAPS device was observed by using the titration measurement.

1. Introduction

The first ion sensitive field-effect transistor (ISFET) with SiO_2 gate as sensing material for bio-medical applications was invented by P. Bergveld in 1970 [1]. A new type of silicon-based sensor, the light-addressable potentiometric sensor (LAPS), which was introduced by Hafeman in 1988, has been receiving much attention owing to its addressability, simple structure, fewer processing steps, low cost, and convenient detection system [2]. Over the past few years, to obtain better pH sensing performance, many high-dielectric constant (high-k) materials, such as Ta_2O_5 and HfO_2 [3-4], with high pH sensitivity and stability have been proposed as sensitive layers. However, for the inorganic high-k materials, it is difficult to sense the anion ions. In this study, the LAPS structure with Sm_2O_3 sensing membrane was proposed to sense the potassium and chloride ions. The nitrogen ions were incorporated into Sm_2O_3 by using the PIII technique, which is an abundant and efficient implantation method. The implantation time was adjusted to change the concentration of implanted nitrogen ions. In KCl solution, the potassium ions can be detected by using the device without treatment. On the other hand, the chloride ion sensitivity can be obtained from the device with the nitrogen PIII treated Sm_2O_3 membrane. The sensitivity was about 35.39 mV/pCl for the nitrogenized Sm_2O_3-LAPS device.

2. Experimental

The LAPS devices were fabricated on 4-inch p-type (100) silicon wafers with first cleaned by standard RCA method. A 50-nm-thick SiO_2 film was thermally grown on Si wafers at 950 ^oC for 100 minutes by dry oxidation. Then, a 10-nm-thick Sm_2O_3 sensing membrane was deposited by RF sputtering with a 99.9% pure samarium target in the ambient of Ar and O_2 mixture. After that, the nitrogen incorporation was performed on the Sm_2O_3 sensing membrane by the PIII system at 5 kV for 1, 3, and 5 minutes, and denoted as W/O, 1 min, 3 min, and 5 min, respectively. Different nitrogen PIII treatment times were taken to obtain different concentration of nitrogen atoms within the samarium oxide. Subsequently, all the samples were treated by the rapid thermal annealing (RTA) in N_2 ambient at 700 ^oC for 30 s. Finally, a 300 nm-thick Al film was deposited by thermal evaporation for backside contact. To define the backside illumination area of LAPS, a wet etching process was used to pattern the Al electrode. The detailed process flow and LAPS measurement system were shown in Fig. 1 and 2 respectively. The Lock-in amplifier was used to be a filter and amplify the received signal. To drive the LED with a wavelength of 890 nm, the ac driving voltage with the frequency of 100 Hz and the amplitude of 5 V was supplied by using a function generator. The output signals were obtained by transforming the photo-currents into photo-voltages through a 15 kΩ resistance between LAPS chip and lock-in amplifier. All samples were immersed in reversed osmosis (RO) water for 12 hours to get a stable pK and pCl sensing response.

3. Results and Discussion

In order to confirm the material properties of the Sm_2O_3 film, the XPS (X-ray photoelectron spectroscopy) was performed. Fig. 3 shows the N 1*s* and O 1*s* XPS spectra of the Sm_2O_3 films with nitrogen PIII treatment. The N *1s* peak at about 404 eV indicated the formation of N-O bond (Fig. 3(a)). Also, the O 1*s* peak at 530.4 and 533 eV indicated that the Sm-O and N-O bonds formation, respectively, as shown in Fig. 3(b). We can also observe that the peak of N-O bond increased with the increase of PIII treatment time. Figure 4 demonstrates the typical *I-V* curves of the nitrogen PIII treated Sm_2O_3 membrane under different KCl buffer solution for LAPS measurement. The sensing behavior of the potassium and chloride ions can be observed from the samples without and with nitrogen PIII treatment respectively. The sensitivity was changed from positive to negative with nitrogen PIII treatment, so we can confirm that the chloride ions were detected. This could be attributed to the generation of positive charges within the Sm_2O_3 after the nitrogen PIII treatment. The positive charges will lead to the V_{FB} shift toward negative direction. The potassium ions were repelled from the sensing membrane and the chloride ions were attracted with the positive charges. Figure 5 displays the sensitivity of potassium and chloride ions of the Sm_2O_3-LAPS devices with and without nitrogen PIII treatment. The optimized chloride ion sensitivity of the Sm_2O_3-LAPS with nitrogen PIII treatment for 3 min was 35.39 mV/pCl. Significant sensitivity change as a function of potassium and chloride ion concentration for the nitrogenized Sm_2O_3-LAPS device was observed by using the titration measurement.

4. Conclusions

In this work, the Sm_2O_3 sensitive membranes treated by nitrogen PIII on the light-addressable potentiometric sensor (LAPS) structure was successfully demonstrated to sense the potassium (K^+) and chloride (Cl^-) ions. The optimized chloride ion sensitivity of the sample with nitrogen PIII treatment for 3 min was 35.39 mV/pCl, which can be used in future biosensor applications.

Acknowledgement

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References

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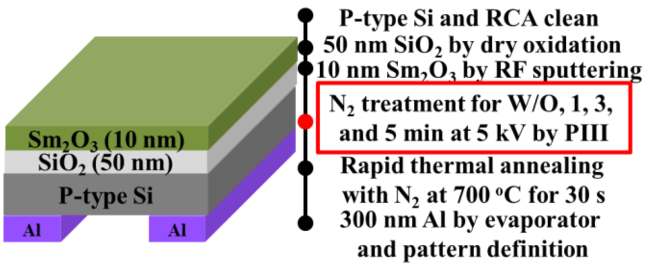

Fig. 1 The schematic structure and process flow of nitrogen PIII treated Sm_2O_3-LAPS device.

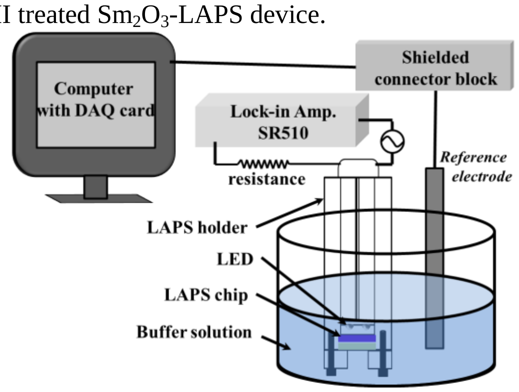

Fig. 2 Typical LAPS measurement system.

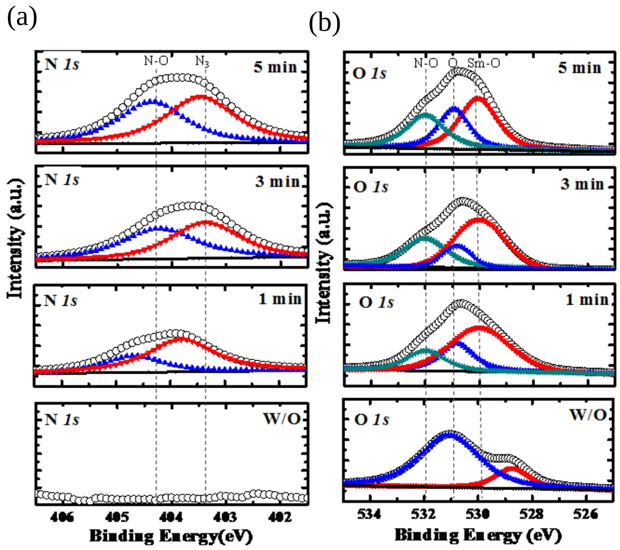

Fig. 2 (a) N 1s and (b) O 1s XPS spectra of the Sm_2O_3 films with nitrogen PIII treatment.

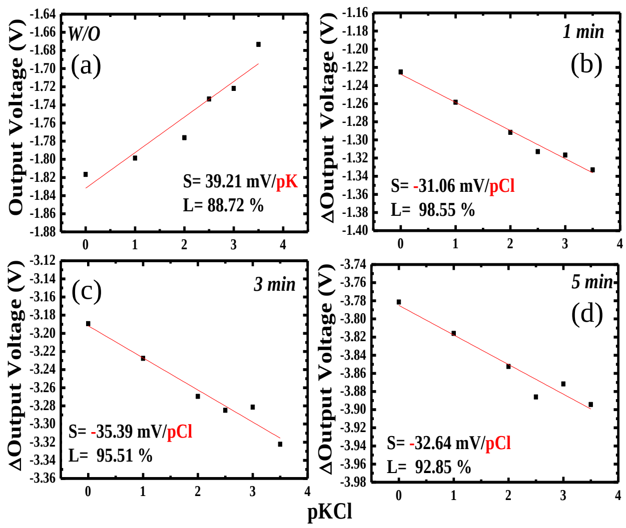

Fig. 4 pKCl-sensitivity and linearity of the Sm_2O_3 LAPS (a) without and with nitrogen PIII treatment for (b) 1 min, (c) 3 min, and (d) 5 min, respectively.

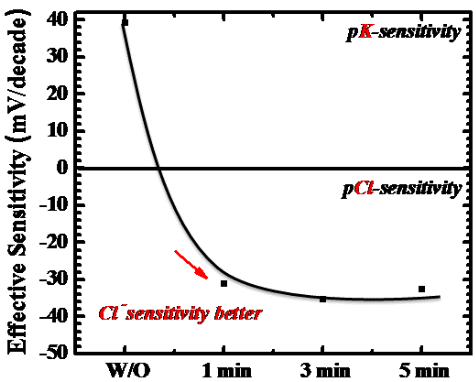

Fig. 5 pKCl-sensitivity of the nitrogen PIII treated Sm_2O_3 LAPS.