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LAPS with nanoscaled and highly polarized HfO_2 by CF_4 plasma for NH_4^+ detection

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ABSTRACT

In this article, the detection of ammonium (NH_4^+) ion using nanoscaled 2-nm thick atomic layer deposition (ALD)-hafnium oxide (HfO_2) films with post rapid thermal annealing (RTA) and carbon tetrafluoride (CF_4) plasma treatments based on light-addressable potentiometric sensor (LAPS) was investigated. 2-nm thick ALD-HfO_2 films with post RTA and CF_4 plasma treatment were fabricated as sensitive membranes, respectively. Measured pNH_4 response from 2-nm thick ALD-HfO_2 LAPS was decreased with increasing annealing temperature and was improved under CF_4 plasma treatment. The optimum pNH_4-sensitivity of 37 mV/pNH_4 was achieved with both 900 °C annealing and 5 min CF_4 plasma on ALD-HfO_2 LAPS. When compared to the same structure without plasma treatment, the sensitivity was improved by approximate fourfold. Based on X-ray photoelectron spectroscopy (XPS) analysis, increased pNH_4-sensitivity was attributed to polar dipole (F—O) formation in ALD-HfO_2 thin films due to the incorporation of fluorine by CF_4 plasma treatment. To assess interferences from other ions (H^+, Na^+, K^+, and Ca^{2+}), selectivity coefficients obtained by fixed interference method (FIM) measurements were presented.

1. Introduction

In order to analyze the changes in concentration in real-time and on-site, many different types of sensors have been proposed over the past decades. Among the proposed sensors, semiconductor based devices, such as ion selective electrodes (ISEs) [1], electrolyte–insulator–semiconductor (EIS) [2], ion-sensitive field-effect transistors (ISFETs) [3], and organic thin-film transistors (OTFTs) [4], have shown processing compatibility with complementary metal-oxide semiconductor (CMOS) technology and exhibited advantages in achieving small, reliable, and robust devices, making them suitable candidates for sensor applications. Recently, a new type of semiconductor based sensors, namely, light-addressable potentiometric sensor (LAPS) with an EIS structure first introduced by Hafeman et al. [5], has received much attention owing to its addressability, surface flatness, and simplicity of fabrication process [6,7]. Fig. 1 shows the schematic of the LAPS structure and the surface of the sensing insulator, which is in contact with the examined electrolytes. A DC bias is applied through the reference electrode to form a depletion layer (space charge region) around the interface between the insulator and the semiconductor. When light irradiates the back-side of the LAPS, the generated electron–hole pairs will be separated by the electric field in the depletion layer, causing a compensatory coupled movement of charges in the external circuit. In addition, a part of induced current is attributed to the diffusion of light-induced charges from the point of generation near the back-side bulk to the depletion layer. These two actions result in the generation of current in the external circuit, which can then be detected by an ammeter [5]. When the chip is immersed in the different concentration solutions, the surface potential depending on the number of binding ions will change the space charge region. As the result, the device threshold voltage shift (sensitivity) can be revealed by monitoring an AC current.

Biosensors for measurements and on-line monitoring of urea concentration are of great interest in biomedical and clinical analysis applications. In clinical diagnostics, the concentration of urea in blood is an important marker of patient's constitution and disease prediction, such as kidney failure [8] and uremic toxin [9]. Recently, to determine the concentration of urea, ammonium (NH_4^+) ion, one of the by-products from the hydrolysis reaction of urea catalyzed by the enzyme (urease), can be detected and quantified [10]. The enzymatic reaction of urea hydrolysis reaction is as follows:

$$NH_2CONH_2 + 3H_2O \xrightarrow{\text{urease}} CO_2 + 2NH_4^+ + 2OH^- \quad (1)$$

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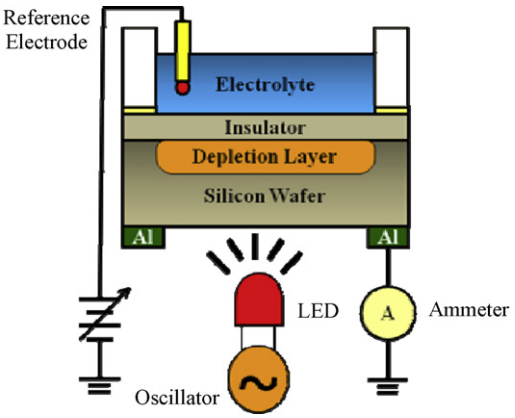

Fig. 1. The structure of LAPS.

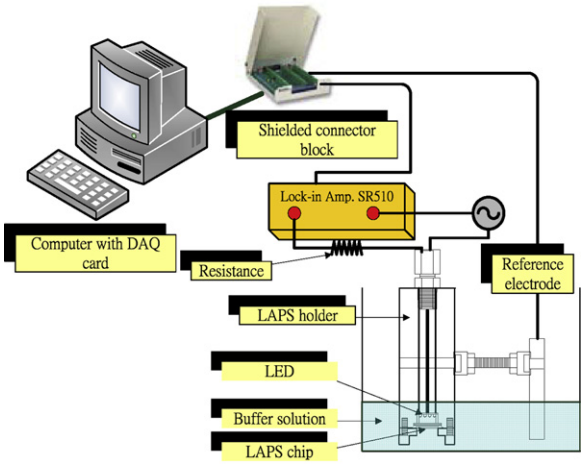

Fig. 2. The LAPS measurement system.

Over the past few years, different types of materials have been proposed to obtain a good sensitivity for the detection of NH_4^+ ion [11,12]. Due to general requirements concerning the minimization of sensor diameters and the increment of their reliability, a high-*k* material, which is compatible with advanced CMOS technology and its higher polarization could attach more ions in the buffer solution, is a potential candidate for preparation of NH_4^+-sensitive layer. In previous works, a single hafnium oxide (HfO_2) layer prepared by sputter system with higher pH sensitivity, low drift, and small body effect was proposed as a promising sensing material for pH detection [13–15]. Recently, our results show that a lower drift effect could be achieved due to the quality of thin film fabricated by ALD system is better than sputter system [16]. However, the unmodified HfO_2 thin film could not be used as a sensitive layer for NH_4^+ ion detection because its sensitivity was not satisfying.

The innovating method presented in this work is the development of a novel functionalization method using rapid thermal annealing (RTA) and carbon tetrafluoride (CF_4) plasma treatments on a 2-nm thick HfO_2 layer grown by atomic layer deposition (ALD) for NH_4^+ ion detection based on LAPS. The CF_4 plasma could be directly applied on the membrane's surface. Moreover, it is very easy to accomplish multi-ions sensing membrane in the LAPS system. Except for the pNH_4-sensitivity, the selectivity coefficients ($K_{NH_4,H}$, $K_{NH_4,Na}$, $K_{NH_4,K}$, and $K_{NH_4,Ca}$) extracted from the basis of the fixed interference method (FIM) measurements are also evaluated. In summary, the possible sensing mechanism based on polarized bonds formation of the 2-nm thick HfO_2 thin film is evident from the material analysis by XPS.

2. Experimental

2.1. Device fabrication

A p-type (1 0 0) Si wafer of 8–12 Ω cm was used as the substrate of the LAPS sensor. Due to the requirement of cost reduction by high throughput, high quality HfO_2 thin film with thickness of 2 nm was chosen as the sensing membrane, without SiO_2, directly upon Si wafer using ALD system. For HfO_2 growth, a metal precursor – tetrakis (ethylmethylamino) hafnium (TEMAH), and an oxidizing agent – vapor of DI water, were used as reactants. Both reactants were carried into the reaction chamber with the purified Ar gas and the substrate temperature of 200 °C. As studied in [17], roughening the structure of an 8-nm thick HfO_2 film surface can be achieved by post RTA. To enhance the roughness of sensing membrane surface, 2-nm thick ALD-HfO_2 LAPS were processed additionally with RTA at 500 °C, 700 °C, and 900 °C in nitrogen ambient for 30 s, respectively. This could create more reactive sites on the surface and increase the possibility of fluorine (F^-) ions' attachment on the surface. In addition, in response to NH_4^+ ion detection, CF_4 plasma post-treatments of 1, 3, and 5 min were performed on the 2-nm thick ALD-HfO_2 LAPS using plasma-enhanced chemical vapor deposition (PECVD) under RF power of 30 W and processing pressure of 500 mTorr with substrate temperature at 300 °C. For electrical signal acquisition from the back-side of the silicon, a 300-nm thick Al layer was evaporated on the back-side of the Si wafer to form the contact. Finally, in order to let the light source penetrate through the Si wafer properly and generate the electron–hole pairs, photolithography and wet etching processes were used to open a window for illumination of LAPS on the back-side Al electrode.

2.2. LAPS measurement system

Fig. 2 shows the schematic of the LAPS measurement system including the reference electrode, measurement cell, lock-in amplifier, and computer with DAQ card. The lock-in amplifier (Stanford Research Systems, model SR510) was used as a filter and an amplifier for the incoming signals. The LED light source of 890 nm wavelength was driven by a function generator that outputs 5 V AC at 100 Hz. An output signal was obtained by transforming the photo-currents into photo-voltages through a 15 kΩ resistance between the LAPS chip and the lock-in amplifier. To obtain output responses in each measured curve, the signals (photocurrent multiplied through resistance) in different biases were automatically calculated using root mean square (RMS) function of self-designed LabVIEW software.

2.3. Data extraction based on inflection point

The inflection points in the second derivatives of the current–voltage (*I–V*) curves measured in different electrolytes were identified as output signals. An inflection point is the intersection between an upward slope and a downward slope of the photovoltages. It could be shifted owing to ion charges changing under different concentrations and resulted in providing different surface potentials. Fig. 3 is a simplified representation of the second differential *I–V* curves of 2-nm thick ALD-HfO_2 LAPS and the inset shows the inflection points, where the zeros of the second differential photovoltage are plotted against the pH values. The sensitivity of 44 mV/pH and the linearity of 99.99% can be obtained by linear fitting.