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Durable nitrate sensor by surface modification

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ABSTRACT

This work presents the development of nitrate sensor based on Ion Sensitive Field Effect Transistor (ISFET) technology to achieve longer device's lifetime. This lifetime depended on the adhesion of PVC ion-selective membrane on the Si₃N₄ sensing membrane of ISFET. The adhesion level directly affected the leaching of plasticizer. Such improvement utilized surface modification techniques by immersing the sensing membrane in the solution of 5% 3-mercaptopropyl-trimethoxysilane (MPTMS)/methanol. The modified surface was detected through the change of hydrophobicity and thickness of MPTMS using the contact angle measurement and ellipsometry techniques. The appropriate time for immersion was 18 h. The modified surface achieved the optimal hydrophobicity with contact angle of 100.32°. The presence of MPTMS film was confirmed by detecting the thiol-group using Fourier Transform Infrared (FTIR) spectrophotometry and Auger Electron Spectroscopy (AES). The PVC ion-selective membrane was then immobilized on the surface to create nitrate sensors with the following characteristics. The Nitrate-Nitrogen detection limit = 2.44 ppm with linear range from 5 to 60 ppm at sensitivity of 56 mV/dec. ($R^2 = 1$). The response time was 90 s. Finally, this nitrate sensor could extend the total utilization lifetime from 8 to 17 weeks.

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1. Introduction

Nitrogen is an important element for plants. There are 3 typical forms of nitrogen found in soil, i.e. Urea, Ammonia, and Nitrate. However plants can only use nitrogen in the form of nitrate. Urea is decomposed by the enzyme urease or chemical hydrolyzed into ammonia and carbon dioxide. The ammonia is then converted by nitrification into nitrate. Therefore, nitrate concentration in soil is a good parameter for monitoring soil fertilization. There are many techniques to measure nitrate, spectrophotometry [1,2], mid-infrared Fourier Transform Spectroscopy [3,4], for examples. However those techniques require complicate sample preparation and are high cost and time-consuming.

This work identifies such problems and proposes another technique to monitor nitrate by mean of developing a nitrate sensor based on an ISFET technology. ISFET was invented by Piet Bergveld in 1970 [5]. ISFET is very similar to metal oxide semiconductor field effect transistor (MOSFET) except there is no metal gate on the gate dielectric. In our case, the gate dielectric was Si₃N₄ [6]. This Si₃N₄ film was acting as a sensing membrane to hydrogen ion. The metal gate was replaced with an external reference electrode for an ISFET. This reference electrode then determined the gate potential for particular hydrogen concentration.

Apart from using Si₃N₄ membrane, other dielectrics were also being used; Ta₂O₅ [7,8], Al₂O₃ [9], and TiO₂ [10]. There were reports of ISFETs also being used for different applications such as biosensor [11], chemical sensor [12] and biomedical sensor [13,14].

By immobilizing a specific ionophore mixed with Poly(vinyl chloride) (PVC) on the Si₃N₄ surface of an ISFET, the ISFET could be applied as nitrate sensing ISFET. PVC is a porous material without ion sites to respond to any ions. In this case, the specific ionophore, mixing with the PVC and also acting as the nitrate ion carrier ionophore, was quarternary ammonium compound (QAC). The QAC allowed measurement range from 1×10^{-5} M to 1×10^{-1} M with sensitivity from 52 to 54 mV/Dec [15,16]. However the drawback of the ionophore mixed with PVC was the poor adhesion of the PVC to Si₃N₄. This caused shorter lifetime of such devices [17].

In order to increase the adhesion of PVC to the Si₃N₄ membrane, and therefore increasing the lifetime, we modified the Si₃N₄ surface with self-assembly monolayer (SAM) of 3-mercaptopropyltrimethoxysilane (MPTMS). This MPTMS will act as a coupling agent [18]. SAM is an arrangement of organic molecule by chemical adsorption of organosilane on a solid substrate. Organosilane has a chemical structure of R_(4-n)-Si-(R'X)_n ($n = 1, 2$), where R is an alkoxy which bonds to hydroxyl-terminated substrate such as Si₃N₄, SiO₂, or metal oxide [19,20].

SAM has been used in many applications such as electrochemistry, biomedical microdevice, and surface function [21,22]. There are 2

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methods for creating SAM. One is chemical vapor deposition (CVD) technique, and the other way is chemical liquid phase (CLP) technique. CLP is an easy technique with long history of widespread usage. The technique itself is simply by immersing the substrate of interest in a SAM containing solution.

This paper presents the MPTMS coating using CLP technique. The purpose was to use the MPTMS as a coupling agent for Si_3N_4 membrane and ionophore mixed PVC. First, the Si_3N_4 membrane substrate was left in a 5% MPTMS/methanol solution for a period of time. Optimum time for ISFET was selected on the basis of the measured contact angle (CA). After film deposition saturated, the methoxy group of MPTMS hydrolyzed at the Si_3N_4 film surface. This created the functional group Si-O-CH_3 on MPTMS which bonded to the hydroxyl-terminated surface of Si_3N_4 . The propyl group of MPTMS could then bond to the ionophore mixed PVC. This report will include the result of the saturated thickness of MPTMS as well as the surface analysis using Ellipsometry, CA, FTIR, and Auger spectroscopy. Finally the performance of the ISFET based nitrate sensor by means of Ionophore mixed PVC sensing membrane will be presented.

2. Experimental

2.1. ISFET sensor fabrication process

N-channel $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectric ISFETs were fabricated on a 6 in. P-type silicon wafer with (100) crystal orientation. The resistivity of the wafer was 20–30 $\Omega\text{-cm}$. The fabrication process was as following. Firstly, the local oxidation of silicon (LOCOS) was created. The anti-punch through implantation was then performed using boron with dose of 6.0×10^{11} ions/ cm^2 . Then the wafer was annealed at 900 °C in nitrogen for 30 min. Source and drain of the ISFET were formed by heavily doped N+ implantation with 5.0×10^{15} ions/ cm^2 of arsenic. The substrate was heavily doped with 3.0×10^{15} ions/ cm^2 of boron and then annealed at 900 °C in nitrogen for 40 min. The gate dielectric stack consisting of the bottom 10 nm of SiO_2 and top 50 nm of Si_3N_4 film were deposited with CVD technique.

Depositing 1000 nm of Inter Layer Dielectric (ILD) was consisting of 500 nm of Plasma-Enhanced Chemical Vapor Deposition (PECVD) oxide and 500 nm of Low-Pressure Chemical Vapor Deposition (LPCVD) Tetraethyl Orthosilicate (TEOS) oxide. The contact holes were etched using plasma etching. The interconnect stack metal consisting of TiN/Al-Alloy/TiN/Ti was deposited using sputtering technique. The wafer was then passivated with Si_3N_4 film. Finally, the gate sensing membrane was then exposed by removing the overlying passivation layer using dry etching. N-channel $\text{SiO}_2/\text{Si}_3\text{N}_4$ gate dielectric ISFETs had been fabricated in lots of many wafers, reproducibility, and high fabrication yield as shown in Fig. 1.

2.2. Chemical and reagent

The following list is the chemicals and reagents used in the experiment: quaternary ammonium salts (Fluka), symmetrical tetradodecylammonium nitrate, poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol) (91:3:6% by weight), 2-nitrophenyloctylether (2-NPOE), 3-mercaptopropyltrimethoxysilane (MPTMS), Tetrahydrofuran (THF > 99%), and analytical grade potassium nitrate from Sigma-Aldrich.

2.3. Nitrate ISFET surface modification

The surface modification of Si_3N_4 sensing membrane by SAM technique was started by cleaning process to remove organic residual at the surface of ISFET by immersing the device in 5% Hellmanex for 10 min. It was then further cleaned by the mixture of 1 M HCl and methanol (50:50 v/v) for 30 min. The device was then immersed in 5% (v/v) of MPTMS in methanol for different periods of time in order to find the

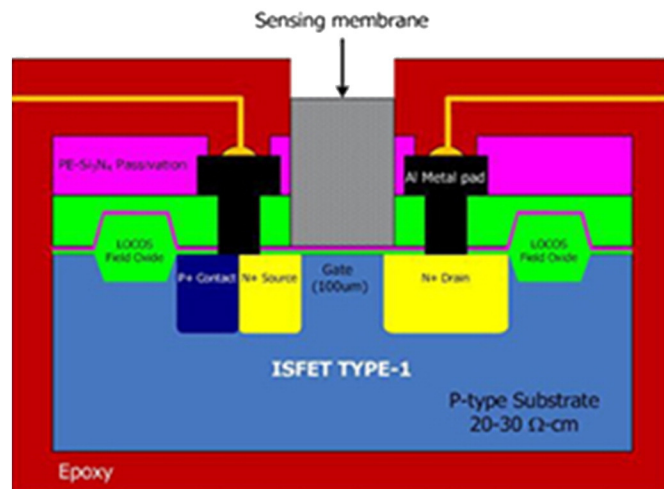


Fig. 1. Schematic of the sensor fabricated on a 6 in. P-type silicon wafer.

suitable time to obtain saturated MPTMS thickness; 1, 3, 6, 9, 12, 18 and 24 h. The PVC membrane solution, consisting of poly(vinyl chloride-co-vinyl acetate-co-vinyl alcohol), (91:3:6% by weight) 29%, 2-NPOE 64%, and quaternary ammonium salts 7%, was dissolved in THF. The surface preparation for PVC membrane coating used the quaternary ammonium salts, namely, tetradodecylammonium nitrate. After that, 10 μL of the PVC membrane solution was dropped on the surface of each ISFET. After leaving them to dry at room temperature in ambient temperature for 24 h, the devices were immersed in KNO_3 solution for 3 h before using them for nitrate measurement.

2.4. Experimental apparatus and measurements

The contact angle (CA) was measured using a goniometer, model 250 from Rame-Hart Instrument Co. (Succasunna, NJ, USA). The sessile drop method was used to determine the static contact angle, θ , of water on Si_3N_4 surface. The result was the average of three different regions on the same surface.

The film thickness of the MPTMS film was measured using a variable angle Spectroscopic Ellipsometer (SE) from VASE, J.A. Woollam Co. (USA). The wavelength range was 700–1500 nm and the incident angle was 70°. The SE measurements were performed based on the relative changes in the amplitude and the phase of a linearly polarized monochromatic incident light upon an oblique reflection from the sample surface. The experimental quantities measured by Ellipsometry are the angles Ψ and Δ , which are related to both the physical thickness and the optical properties of the samples [23–25]. The experimental data are defined in the ellipsometric ratio, ρ , as follows:

$$\rho = \frac{R_p}{R_s} = \tan\Psi e^{i\Delta}$$

where,

R_p = complex reflection coefficients of the light polarized parallel to the plane of incidence.

R_s = complex reflection coefficients of the light polarized perpendicular to the plane of incidence.

$\tan\Psi$ = amplitude ratio of light intensity

Δ = phase difference that develops between the s- and p-wave components after reflection.

The proposed physical model corresponding to each film sample was directly associated with the Cauchy optical dispersion. In the physical model, a multi-layer physical structure (MPTMS layer/ Si_3N_4 (30 nm-thick) layer/ SiO_2 (10 nm-thick)/Si substrate) was assumed with homogeneity and the film's surface roughness was ignored. The

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