Time-Dependent Sensitivity Tunable pH Sensors Based on the Organic-Inorganic Hybrid Electric-Double-Layer Transistor

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Abstract: In this study, we propose tunable pH sensors based on the electric-double-layer transistor (EDLT) with time-dependent sensitivity characteristics. The EDLT is able to modulate the drain current by using the mobile ions inside the electrolytic gate dielectric. This property allows the implementation of a device with sensitivity characteristics that are simply adjusted according to the measurement time. An extended gate-type, ion-sensitive, field-effect transistor consisting of a chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT transducer, and an SnO$_2$ sensing membrane, were fabricated to evaluate the sensing behavior at different buffer pH levels. As a result, we were able to achieve tunable sensitivity by only adjusting the measurement time by using a single EDLT and without additional gate electrodes. In addition, to demonstrate the unique sensing behavior of the time-dependent tunable pH sensors based on organic–inorganic hybrid EDLT, comparative sensors consisting of a normal FET with a SiO$_2$ gate dielectric were prepared. It was found that the proposed pH sensors exhibit repeatable and stable sensing operations with drain current deviations <1%. Therefore, pH sensors using a chitosan electrolytic EDLT are suitable for biosensor platforms, possessing tunable sensitivity and high-reliability characteristics.

Keywords: ion-sensitive field-effect transistor (ISFET); tunable sensitivity; organic–inorganic electric-double-layer transistor; chitosan electrolyte; extended gate; amorphous oxide semiconductor

1. Introduction

pH biosensors are extensively used in various fields, such as disease diagnosis, soil or water quality measurements, the food industry, and chemical research (e.g., the optimal pH value of blood ranges from 7.35 to 7.45) [1–3]. In particular, the ion-sensitive field-effect transistor (ISFET)-based electrochemical pH sensor has been actively studied, owing to its compact size, complementary metal-oxide-semiconductor process compatibility, easy integration capability, low cost, and label-free detection of analytes [4,5]. The gate electrode of a typical ISFET is replaced with an ion-sensitive membrane and an electrolyte solution grounded by a reference electrode. In this structure, ions in the electrolyte bound to the ion-sensitive membrane change the surface potential of the membrane, which is transduced as a decipherable electrical signal through the FET [6,7]. In addition, many studies have reported on extended-gate ISFET (EG-ISFET)-based pH sensors in which the detector (sensing membrane) and the transducer (FET) are separated [8–10]. Conventional ISFETs have a problem in that the sensing membrane of the detector is damaged continuously when exposed to pH buffers. However, EG-ISFET provides a cost-effective sensor platform because it can easily replace damaged detectors and reuse transducers [11]. Meanwhile, electric-double-layer transistors (EDLTs) are drawing attention because they can accumulate high-charge-carrier densities by extremely strong EDL gating [12,13]. Mobile ions inside the gate insulating electrolyte readily migrate to the channel/electrolyte interface, owing to the gate bias to form an EDL, which functions as a nanogap capacitor, thus contributing to a high-gate capacitance and inducing a lower operating voltage [14,15]. Furthermore, the
gradual migration and accumulation of mobile ions by the gate bias continuously alters the channel conductance of the FET [16]. Owing to these unique features, many studies have been conducted to apply EDLT to artificial synaptic devices or biochemical sensor platforms [17,18].

In this study, we propose a pH sensor platform and sensing mechanism with tunable sensitivity by using an EDLT as a transducer for EG-ISFETs. In practical applications, pH sensors with tunable sensitivity are advantageous for conducting measurements over a wide variety of pH ranges, either narrow or wide [19]. In general, ISFETs operating in the quasistatic mode have only a fixed sensitivity. In contrast, to achieve tunable sensitivity, many studies have been reported that have focused (among others) on additional configurations of the gate electrode or on different designs of the sensing area of the device [20–22]. However, these additional components adversely affect device integration and cost-effectiveness. The pH sensor platform that uses the EDLT proposed in this study is able to easily tune the sensitivity by only adjusting the measurement time. Given that the EG and the EDLT are electrically connected, the surface potential that depends on the pH level of the sensing membrane is delivered to the gate electrode of the EDLT. As a result, the migration of ions in the electrolyte depends on the pH level of the buffer, which causes a difference in the drain current of the EDLT in response to the pH level. By utilizing these distinctive characteristics, it is possible to implement pH sensing and facile sensitivity tuning. We fabricated chitosan/Ta$_2$O$_5$ hybrid dielectric EDLTs and measured their basic electrical properties (Figure 1b). The drain current response of the pH sensor composed of the prepared EDLT and EG according to the pH level of the buffer solution was then measured. Finally, modulation of the drain current and tuning of the sensitivity by pulse duration were demonstrated as intended, achieving a tunable pH sensor. These distinctive operations of the pH sensor by using EDLT were verified by comparison with devices composed of a normal SiO$_2$ dielectric FET with the same structure. In addition, the repeatability and stability of the sensing operation of the pH sensor using EDLT were evaluated.

Figure 1. (a) Schematic in three-dimensions and in cross-section. (b) Optical microscopic image of the fabricated chitosan/Ta$_2$O$_5$ hybrid dielectric electric-double-layer transistor (EDLT). (c) SnO$_2$ extended gate (EG) on ITO/glass substrate.
2. Results and Discussion

The Fourier transform infrared spectroscopy (FT-IR) outcome of the solid-state chitosan electrolyte, which plays a key role in EDLT, is shown in Figure 2a. The inset indicates the structure of the molecules constituting the chitosan electrolyte. Chitosan shows bands at approximately 3355 and 2860 cm\(^{-1}\) attributed to O–H and C–H stretching, respectively. Additionally, the bands at approximately 1645, 1529, and 1053 cm\(^{-1}\) were caused by the amide I, amide II, and C–O–C groups, respectively [23–25]. These groups facilitate the migration of hydrogen ions (protons) in the chitosan electrolyte [26]. The fundamental electrical characteristics of the chitosan/Ta\(_2\)O\(_5\) hybrid dielectric EDLT are presented in Figure 2c. Figure 2b shows the transfer curve (\(I_D-V_G\)) measured by double sweeping of the gate voltage \(V_G\) from -15 to 10 V at a constant drain voltage of \(V_D = 1\) V. It can be observed that the transfer curve exhibits the counterclockwise hysteretic loop typically observed in electrolyte-based EDLTs, and it has a hysteretic window of 10.1 V [27,28]. This hysteretic loop is induced by the slow polarization of mobile protons in the chitosan electrolyte [29]. When a positive voltage is applied to the gate electrode, protons in the chitosan electrolyte migrate near the channel of the EDLT, thus inducing charge carriers and increasing the conductance of the channel. The migrated protons are fully depolarized, with a sufficient negative voltage in the backward sweep and return to their initial state. This hysteretic effect is a unique property rarely observed in typical FETs with SiO\(_2\) gate dielectrics, thus allowing EDLTs to mimic biological synaptic behavior. Figure 2c shows the output curve (\(I_D-V_D\)) measured by sweeping \(V_D\) from 0 to 4 V and \(V_G-V_{TH}\) from 0 to 10 V. The \(I_D\) increased linearly in the low-\(V_D\) region and gradually saturated in the high-\(V_D\) region, thus indicating ohmic characteristics at the source/drain contact.

For further investigation of the proton ionic polarization in chitosan electrolytes, transfer curves at various maximum \(V_G\) values were measured, and dynamic \(I_D\) responses to pulse durations were evaluated. As shown in Figure 3a, the double-sweep transfer curves were measured by increasing the maximum \(V_G\) from 0 to 10 V (in increments of 1 V). The threshold voltages (\(V_{th}\)) and hysteretic windows extracted from the measured transfer curves are shown in Figure 3b. The hysteretic window linearly increased with a slope of 0.83 V/V, and a high linearity of 99.02% was achieved as the maximum \(V_G\) value increased. As the maximum \(V_G\) increases, more mobile ions migrate to the chitosan/channel interface, which requires an increased gate voltage to depolarize them again [30], thus resulting in a gradual increase in the hysteretic window. Meanwhile, \(V_{th}\) remained almost constant despite the increase in \(V_G\), owing to the full depolarization of protons by sufficient negative gate bias. Figure 3c shows the dynamic \(I_D\) response to a gate pulse (\(\Delta V = 1\) V) at various pulse durations from 1 to 10 s. Given that the ionic polarization of protons induces electrons into the channel, the \(I_D\) gradually increases while a positive gate pulse is applied. In addition, the peak value of \(I_D\) increased at longer pulse durations. In contrast, the
characteristics of increasing hysteresis and $I_D$ response were not observed in normal FETs of the SiO$_2$ gate dielectric with only dipole polarization (Figure S2). These results indicate that the $I_D$ of the chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT changes depending on the amplitude and duration of the gate voltage.

Figure 3. (a) Double-sweep transfer curves of the chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT at increasing maximum $V_G$; (b) threshold voltage and hysteresis window extracted from the transfer curves; (c) dynamic $I_D$ responses to gate pulses of various durations.

Figure 4 shows a schematic of the proposed time-dependent sensitivity tunable pH sensing system consisting of an EG detector and a chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT. In this sensing system, the electrical signal for pH sensing is sequentially transferred to the gate electrode of the EDLT through the Ag/AgCl reference electrode, the pH buffer solution, the SnO$_2$ sensing membrane, and the ITO electrode of the EG. According to the site binding model, the surface potential ($\psi$) of the SnO$_2$ sensing film can be determined by the chemical sensitivity of a given surface and the number of ions in the pH solution as shown in Equation (1) [31,32]:

$$\psi = 2.303 \frac{kT}{q} \frac{\beta}{\beta + 1} (pH_{pzc} - pH),$$  

where $k$ is the Boltzmann constant, $q$ is the elementary charge, $T$ is the absolute temperature, $\beta$ is the chemical sensitivity of the sensing membrane, and $pH_{pzc}$ is the pH level at which the charge is zero. Additionally, this change in surface potential ($\Delta \psi$) arises depending on the pH level of the buffer solution. The most common sensing method, the quasistatic detection mode, detects the pH level through the transfer curve shift induced by $\Delta \psi$ of the FET [33,34].

Figure S3 shows the transfer curves and reference voltage shift ($\Delta V_R$) for various pH buffer solutions. The transfer curve shifted in a positive direction as the pH decreased, regardless of the transducer. The pH sensitivities in quasistatic mode for the EDLT (with chitosan/Ta$_2$O$_5$ hybrid gate dielectric) and the normal FET (with SiO$_2$ gate dielectric) were similar and equal to 50.17 and 51.72 mV/pH, respectively. Note that these sensitivities are fixed values for the same sensing system unless an additional parameter is provided, such as a second gate voltage. In contrast, the sensitivity can be easily changed in the dynamic sensing mode by using the EDLT and electrical pulses proposed in this study. Based on $\psi$ for pH7, $\Delta \psi$ is a positive voltage in a cation-abundant acidic buffer solution, and a negative voltage in an anion-abundant basic buffer solution. A positive or negative surface potential is superimposed on the electrical sense pulse ($V_{in}$), thus changing the amplitude of the effective pulse reaching the EDLT. Given that the $I_D$ depends on the amplitude and duration of the gate pulse, as illustrated in Figure 3, the peak of the $I_D$ is determined by the pH level and the duration of the sensing pulse. Owing to these unique features of the proposed sensing system, the chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT-based pH sensor has tunable pH sensitivity by adjusting the duration of the gate pulse.
Figure 4. Schematic of a time-dependent pH sensor configured with a tunable chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT and an EG.

To evaluate the pH-sensing behavior, we measured the dynamic $I_D$ response of chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT in various pH buffers. Figure 5a shows the $I_D$ response of a chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT upon application of a gate pulse with an amplitude ($\Delta V$) of 1 V and a duration ($\Delta t$) of 1 s. Given that the IGZO channel of EDLT has n-type properties, the $I_D$ response was higher in the cation-abundant acidic buffer ($\Delta \psi > 0$) than in the anion-abundant basic buffer ($\Delta \psi < 0$) [35]. In addition, the $I_D$ gradually increased owing to the continuous migration of protons during the pulse duration, and the difference in $I_D$ depends on the pH level. Figure 5b shows the change in current between the start ($I_{p0}$) and end ($I_p$) of the $I_D$ at a gate pulse duration of 1 s, whereby the $I_p - I_{p0}$ value decreased from 39.51 nA (pH 3) to 20.62 nA (pH 10) as the pH increased. Although the amplitude and duration of the external pulses were the same, effective pulses of different amplitudes were entered into the transducer owing to the surface potential caused by the pH buffer solution. Meanwhile, the pH-level-dependent pulse changed the $I_p - I_{p0}$ value (as documented by the $I_D$ increasing rate with respect to the pulse duration). The longer the pulse duration is, the greater the difference is in the final $I_p$ according to the pH level. This is an important property for adjusting the pH sensitivity in this study. Similarly, when a normal FET with a SiO$_2$ gate dielectric was used as a transducer, the $I_D$ response was higher in acidic solutions (Figure S4). However, except for a slight change in $I_D$ induced owing to charge trapping, a normal FET without mobile protons has a constant $I_p - I_{p0}$ value (~2.08 nA) close to zero, regardless of the pH value. To evaluate the pulse duration dependence in the pH sensing operation, external pulses (fixed amplitude) with different durations were applied to the Ag/AgCl reference electrode in three types of buffer solutions. Figure S5 shows the $I_D$ responses in buffers with pH values of 3, 7, and 10, with a continuously increasing drain current as a function of pulse duration, thus reaching higher values in more acidic buffers.

Figure 6a shows the modulation of $I_p$ for gate pulses ($\Delta V = 1$ V) with different durations in various pH buffers. The $I_p$ value was obtained from the end of $I_D$ in terms of the gate pulse duration in each measurement; this value increased at lower pH levels and longer pulse durations. Figure 6b shows the pH sensitivity as the slope of $I_p$ with respect to the pH level as a function of the gate pulse duration of the chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT pH sensor. The pH sensitivities were 27.99, 32.25, 38.09, 42.49, and 48.71 nA/pH for pulse durations of 1, 3, 5, 7, and 10 s, respectively, amplified up to 174% without adding electrodes or changing the design of the device. In contrast, in the
normal FET pH sensor with a SiO₂ gate dielectric, a constant Iₚ determined by the pH level was observed, regardless of the pulse duration, as shown in Figure S6. Thus, a pH sensor configured by a normal FET has a fixed pH sensitivity of 43.39 nA/pH, a feature typically found in FET-type pH sensors. Accordingly, the time-dependent Iₚ modulation nature of EDLT enabled the implementation of a unique, sensitivity-tunable pH sensor.

![Figure 5](image1.png)

**Figure 5.** (a) Dynamic Iₚ response in various pH buffer solutions; (b) pH-dependent changes in Iₚ (Iₚ–Iₚ₀) at a gate pulse (1s duration) of the chitosan/Ta₂O₅ hybrid dielectric EDLT.

![Figure 6](image2.png)

**Figure 6.** (a) Modulation of Iₚ for a gate pulse and (b) pH sensitivity as a function of the pulse duration of the chitosan/Ta₂O₅ hybrid dielectric EDLT in various pH buffers.

One of the fundamental requirements for a sensor is the reliability of maintaining a constant sensitivity for repetitive and prolonged sensing operations. In particular, for EG-ISFET-based pH sensors, changes in electrical properties and sensitivity may be affected by defects in the EG membrane or gate insulator of the transistor [36]. Therefore, we measured hysteresis and drift responses to evaluate the repeatability, reliability, and stability of pH sensors fabricated using a chitosan/Ta₂O₅ hybrid dielectric EDLT. The ion migration of the chitosan electrolyte enabled the unique pH sensitivity control, but the long-term memory effect induced by the migrated ions may lead to the deterioration of the stability and reliability. Hence, for initialization of this unwanted long-term memory effect, we used a pair of sensing pulses (1 V, 1 s) and erasing pulses (–0.5 V, 1 s) as one pulse cycle. Figure 7 shows the reliability and stability of the chitosan/Ta₂O₅ hybrid dielectric EDLT pH sensors evaluated subject to this condition. The hysteretic effect induced by repeatedly...
changing the pH buffers according to the hysteretic loop of pH 7 → 4 → 7 → 10 → 7 is shown in Figure 7a. The inset shows single cycles of gate pulses used for hysteresis and drift measurements. The difference in $I_p$ values between the first and third pH 7 cycles (hysteretic width) is 0.55 nA, and the deviation is 0.38%, thus showing good repeatability and stability [37,38]. Figure 7b shows the drift response for $I_p$ measured for 600 s in a pH 7 buffer solution, with no abrupt changes in $I_p$ even after long-term operation. The coefficient of variation extracted from this result (based on the standard deviation ($\sigma$) and average ($\mu$)) was 0.77%, with a good stability and reliability of less than 1% [39,40]. As a result, the pH sensor (which used an EDLT) with tunable sensitivity characteristics proposed in this study successfully demonstrated excellent repeatability, stability, and reliability values < 1%.

![Figure 7](image_url)  
**Figure 7.** (a) Hysteretic and (b) drift responses of a time-dependent pH sensor by using a chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT.

3. Materials and Methods

3.1. Chitosan Electrolyte Solution Synthesis

The chitosan electrolyte solution was prepared by dissolving chitosan powder and acetic acid. The 2 wt% chitosan powder (>75% deacetylated, Sigma-Aldrich, City, State (if applicable), Country) obtained from shrimp shell was dissolved in a 2 wt% acetic acid solution and diluted with deionized water. The mixture was blended at 50 °C at 800 revolutions per minute in a magnetic stirring system. The solution was then filtered through a polytetrafluoroethylene syringe filter with a 5 µm pore size to obtain a clear and homogeneous solution.

3.2. Fabrication of the Chitosan–Ta$_2$O$_5$ Hybrid EDLTs as Transducer

As a starting material, a p-type silicon wafer on which a 100 nm-thick SiO$_2$ layer was thermally grown was cleaned by a standard Radio Corporation of America (RCA) process. A 50 nm-thick a-IGZO channel layer was deposited by radio frequency (RF) magnetron sputtering subject to the following conditions: RF power: 100 W; working pressure: 6 mTorr; and Ar gas flow: 30 sccm. The active area of the a-IGZO channel layer was defined by photolithography and a wet etching process by using a 30:1 buffer oxide etchant with channel length (L) and width (W) of 10 µm and 20 µm, respectively. A 150 nm-thick Ti source/drain electrode was deposited via an e-beam evaporator and patterned by a liftoff process. The prepared chitosan electrolyte solution was spin-coated on the devices, dried, and oven-baked at 130 °C for 10 min. Subsequently, an 80 nm-thick Ta$_2$O$_5$ barrier layer was deposited by RF magnetron sputtering to prevent chemical and mechanical damage, which enables a photolithography process for an organic chitosan electrolyte [41]. A 150 nm-thick Al layer was deposited by an e-beam evaporator and patterned through a lift-off process on the chitosan–Ta$_2$O$_5$ hybrid EDL gate dielectric as the top gate electrode. Finally, the source/drain contact holes were etched by a reactive ion etching system. The three-dimensional (3D) schematic and cross-sectional structure and the photograph of the fabricated chitosan/Ta$_2$O$_5$ hybrid dielectric EDLT are shown.
in Figures 1a and 1b, respectively. In addition, to verify the unique sensing capability of
the proposed pH sensor using EDLT, we also prepared normal FET devices with the same
structure in which the gate dielectric (chitosan–Ta
$_2$O$_5$ hybrid EDL) was replaced, with SiO$_2$
with a thickness of 100 nm. A schematic of the cross-sectional structure of the normal FET
and a photograph of the fabricated device are shown in Figure S1.

3.3. Fabrication of the Extended Gate as Sensing Membrane

The extended gate (EG) was fabricated on a transparent glass substrate (1.5 cm × 2.5 cm).
A 300 nm-thick indium tin oxide (ITO) conductive layer was deposited by using RF magnetron
sputtering. A 50 nm-thick SnO$_2$ sensing membrane was deposited by RF magnetron sputtering
subject to the following conditions: RF power: 50 W; working pressure: 3 mTorr; and Ar
gas flow: 20 sccm. A polydimethylsiloxane (PDMS) reservoir with a diameter of 0.6 cm
was attached to the SnO$_2$ sensing membrane to inject and store the pH buffer solution.
A photograph and the cross-sectional structure of the fabricated transparent EG are shown
in Figure 1c.

3.4. Device Characterization

The current-voltage characteristics of the fabricated chitosan–Ta$_2$O$_5$ hybrid EDLT-
based ISFET sensor were evaluated by using an Agilent 4156B precision semiconductor
parameter analyzer. To evaluate the sensing behavior of the configured pH sensors, electrical
pulses were applied to the EG by using an Agilent 8110A pulse generator. As a
reference electrode, a commercially available Ag/AgCl electrode (Horiba 2080A-06T) was
used for pH detection. All measurements were performed at room temperature, a relative
humidity of ~25%, and the device was placed in a dark box during measurements to avoid
electrical/optical noise.

4. Conclusions

In this study, a sensitivity tunable pH sensor composed of an EDLT with a chitosan/Ta$_2$O$_5$
hybrid gate dielectric was proposed. The mobile protons in the chitosan electrolyte of the EDLT
migrated, owing to the gate voltage, and affected the $I_D$. Because the electrical signal was
transferred to the EG via a pH buffer solution, the number of migrated ions depended on the
pH level and the gate pulse duration. This distinctive feature and dynamic sensing operation
allowed the proposed pH sensor to easily adjust the sensitivity without additional gate
electrodes or device-design changes. In EG-ISFETs composed of an SnO$_2$ sensing membrane
and EDLT, the maximum $I_D$ ($I_p$) response to gate pulses increased with decreasing pH level,
and the growth rate of the $I_p$ also improved as the pulse duration increased. Specifically,
the sensitivity can be facilely adjusted, depending on the pulse duration, and can increase
up to 174%, from 27.99 to 48.71 nA/pH. These characteristics were not observed in normal
FETs (with SiO$_2$ gate dielectrics) built for comparison, thus indicating that they are inherent in
pH sensors with EDLT. We also evaluated the hysteresis and drift response of a pH sensor
with EDLT, and demonstrated excellent repeatability, stability, and reliability values < 1%. As
a result, the EG-ISFET-type pH sensor comprising the EDLT transducer is expected to be a
useful biosensor platform with a simple tunable sensitivity and reliable sensing operation.

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