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Full Length Article

Improving pH sensitivity by field-induced charge regulation in flexible biopolymer electrolyte gated oxide transistors

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ABSTRACT

Electrical manipulation of charged ions in electrolyte-gated transistors is crucial for enhancing the electric-double-layer (EDL) gating effect, thereby improving their sensing abilities. Here, indium-zinc-oxide (IZO) based thin-film-transistors (TFTs) are fabricated on flexible plastic substrate. Acid doped chitosan-based biopolymer electrolyte is used as the gate dielectric, exhibiting an extremely high EDL capacitance. By regulating the dynamic EDL charging process with special gate potential profiles, the EDL gating effect of the chitosan-gated TFT is enhanced, and then resulting in higher pH sensitivities. An extremely high sensitivity of ~57.8 mV/pH close to Nernst limit is achieved when the gate bias of the TFT sensor sweeps at a rate of 10 mV/s. Additionally, an enhanced sensitivity of 2630% in terms of current variation with pH range from 11 to 3 is realized when the device is operated in the ion depletion mode with a negative gate bias of −0.7 V. Robust ionic modulation is demonstrated in such chitosan-gated sensors. Efficiently driving the charged ions in the chitosan-gated IZO-TFT provides a new route for ultrasensitive, low voltage, and low-cost biochemical sensing technologies.

1. Introduction

Precise control over transport, delivery and polarization of ions and molecules in field effect transistor (FET) configurations is of great significance in the fields of biosensing and bionics [1–4]. As an ion modulating device, electrolyte-gated transistor (EGT) has attracted intense attention for biochemical sensing detections due to the huge ionic electric-double-layer (EDL) gate capacitance [5–8]. In the EGT-based sensor, essentially speaking, trace amounts of charged species adsorbed on the sensing gate give rise to significant variations in channel current by the EDL gating effect. Due to the field-induced ion transport in the formation of EDL, the EDL gating effect is mostly governed by the dynamic interfacial charging process [9,10]. Thus, efficiently driving the ion transport in EGTs with special gate potential profiles is meaningful for maximizing the function of EDL gating, which is expected to further improve the intrinsic sensitivity of the EGT sensors. So far, much effort has been devoted to the development of ultrasensitive biosensors based on EGT devices [11,12]. In our previous studies, a type of oxide-based thin-film transistor (TFT) gated by inorganic solid electrolyte has been used as low-voltage biochemical sensors. Remarkable sensing abilities have been demonstrated on such EGTs with various architectures [13,14]. However, the improvement of sensing abilities for the reported EGT sensors is mostly realized by the complicated surface engineering and device architecture innovation [15,16]. The inherent influence of dynamic charge regulation at the electrolyte/channel interface on the sensing properties of EGT devices is still unexplored.

On the other hand, natural polymer materials, benefit from widely existing in the nature and low-cost volume fabrication, have received considerable interests in the development of new electronic materials. Chitosan is a biodegradable, biocompatible and nontoxic amine-riched polymer, which has been widely utilized in the fabrications of biomedical materials and electrochemical biosensors [17,18]. Due to its high ionic conductivity resulting from the protonation of amines by acid doping, as illustrated in Fig. 1, chitosan film can also be employed as a solid electrolyte membrane [19,20]. In addition, based on the superior film forming ability, chitosan film can be printed easily on flexible substrates, enabling irregular-shaped sensing applications.

In this work, solution-deposited chitosan films were used as dielectric in flexible indium-zinc-oxide (IZO)-based TFTs for pH sensing applications. The dynamic characteristics of EDL gating were studied by regulating the rate of the linear gate voltage ramps applied to the chitosan-gated IZO-TFTs. Much stronger gating effect was obtained for the chitosan-gated IZO-TFTs when the gate volt-

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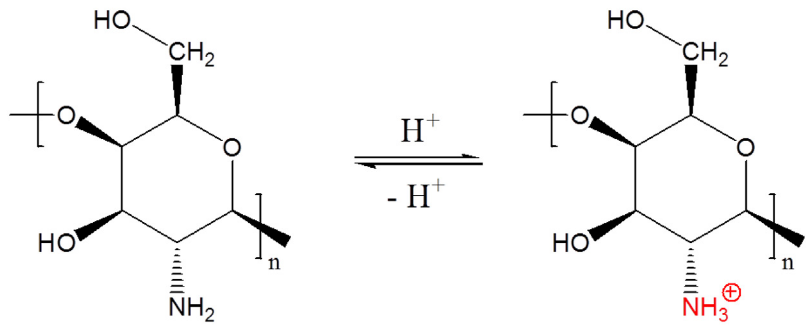

Fig. 1. The mechanism of protonation/deprotonation process for chitosan.

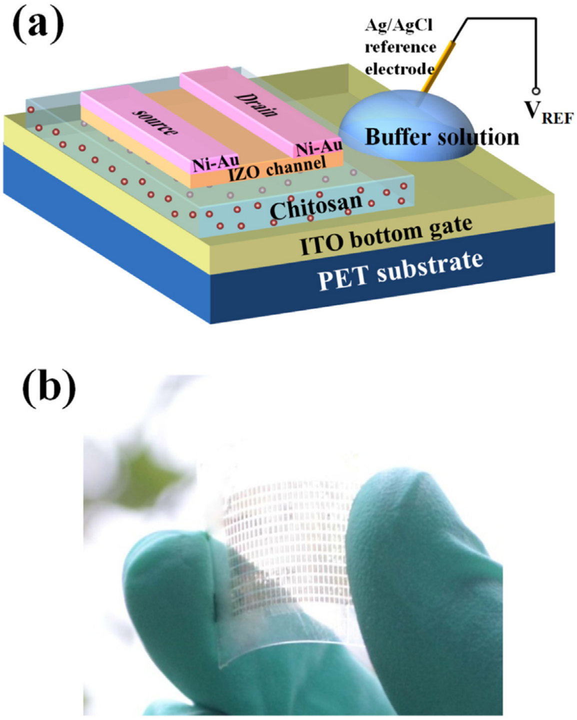

Fig. 2. (a) Schematic image of the chitosan-gated IZO-based TFT pH sensor. (b) The picture of the sensor array fabricated on a flexible PET substrate.

age swept at a low rate. An ultrahigh sensitivity of ~57.8 mV/pH close to Nernst limit was achieved by sweeping the gate voltage at a rate of 10 mV/s. In addition, an enhanced EDL gating effect was observed when the chitosan-gated TFT sensor worked in the ion depletion mode, leading to an improved sensitivity of 2630% in terms of current variation from pH = 11 to pH = 3 with a negative gate bias of −0.7 V. Regulating the charged ions by gate electric field in such flexible chitosan-gated IZO-TFTs plays a crucial role in their applications of ultrasensitive, low-cost portable biochemical sensors.

2. Experimental

The chitosan-gated IZO-TFT sensors were fabricated on PET plastic substrates at room temperature, as schematically shown in Fig. 2a. First, 200 nm thick indium-tin-oxide (ITO) layer was deposited as bottom gate on the PET substrates by magnetron sputtering method, and then a sensing ITO area of 5.0 mm × 5.0 mm was shielded by an adhesive tape until the whole fabrication process was finished. Next, the chitosan solution (4 wt% in acetic acid) was directly drop-casted onto the ITO conductive PET substrate or silicon wafer and dried in air to form a film. Thirdly, patterned IZO channel layer with a thickness of ~30 nm were deposited by magnetron sputtering method with the aid of a nickel shadow mask. Channel length (L) and width (W) is 80 μm and 1000 μm, respectively. The isolated IZO patterns were also deposited on chitosan film coated ITO conductive PET substrate to obtain an IZO/chitosan/ITO capacitor. Finally, Ni/Au (30/50 nm) stack films used as the source/drain electrodes were deposited by e-beam evaporation method through another nickel shadow mask. Fig. 1b shows the photo of the bent IZO-TFT arrays gated by the chitosan films on a PET substrate. The thickness and the cross-sectional profile of chitosan films were measured by a field-emission scanning electron microscope (SEM, Hitachi S-4800). Proton conductivities and frequency dependent capacitances of the chitosan films were characterized by a Solartron 1260A impedance analyzer. Transistor characteristics of the device were recorded by a semiconductor parameters characterization system (Keithley 4200 SCS) at room temperature. The dynamic responses of EDL gating based on field-induced ion transport were analyzed by sweeping the gate voltage at different rates. The pH sensing performances of the device were measured by the same system with a miniature Ag/AgCl reference electrode dipped into a 10 μL phosphate buffer solution droplet dropped on the sensing area. The pH buffer solution was prepared by titrating 0.01 M phosphate solution with dilute hydrochloric acid or potassium hydroxide solution. The pH value was monitored by a commercial pH meter. Electric measurements were performed in a dark box to prevent interference from the visible light.

3. Results and discussion

Fig. 3a shows the cross-sectional SEM image of the chitosan-based proton-conductive film on a Si (100) substrate. The thickness of chitosan film is estimated to be ~7 μm. The inset in Fig. 3a shows the enlarged cross-sectional mircoscopy image. A loose microstructure with nanopores is observed. Proton conductivities (δ) of the chitosan films were measured with sandwiched IZO/chitosan/ITO structures, as shown in the inset of Fig. 3b. The impedance spectroscopy data are collected as real (Re Z′) and imaginary (Im Z″) components of the complex impedance. A typical Cole–Cole plot is observed in Fig. 3b. The impedance real value (R) where the impedance imaginary value is zero is used to obtain the δ value by using the following relation [21]:

$$\delta = \frac{D}{(R - R_0)A} \quad (1)$$

where D, A and R_0 are the thickness of the chitosan film, the electrode surface area and the resistance of electrode, respectively. In our case, the thickness D is ~7 μm, A is ~1.5×10^{-3} cm^2 while R_0 is measured to be ~30 Ω. Thus, δ is estimated to be ~2.8×10^{-3} S/cm, indicating that the chitosan film shows high proton conductivity at room temperature. The leakage current (I_G) of the chitosan film was