Organic Electronics 56 (2018) 82–88

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Organic/inorganic hybrid low-voltage flexible oxide transistor gated with biodegradable electrolyte

Wan Tian Gao[a,b,d], Li Qiang Zhu[b,d,*], Hui Xiao[b,d,**], Fei Yu[b,c,d], Jian Tao[b,d], Dong Yun Wan[a], Ju Mei Zhou[e]

[a] School of Material Science & Engineering, Shanghai University, Shanghai 200444, People's Republic of China
[b] Key Laboratory of Graphene Technologies and Applications of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, Zhejiang, People's Republic of China
[c] Nano Science and Technology Institute, University of Science and Technology of China, Suzhou 215123, People's Republic of China
[d] University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China
[e] Faculty of Maritime and Transportation, Ningbo University, Ningbo 315211, Zhejiang, People's Republic of China

ARTICLE INFO

Keywords:
Organic/inorganic hybrid
Electrical double layer (EDL)
Eco-friendly "green" electronics

ABSTRACT

Eco-friendly "green" electronics are attracting increasing interests in recent years. Here, biodegradable organic/inorganic hybrid indium-tin-oxide electric double layer (EDL) transistors were fabricated on plastic substrates. Solution processed chitosan based polysaccharide films were used as gate dielectrics. Due to extremely high EDL capacitances of the chitosan-based electrolytes, the oxide EDL transistors exhibit good performances. Resistor loaded inverters were also built, exhibiting full-swing characteristics and high voltage gains at low operation voltages. Wave-type conversions were realized including conversions from sinusoid waves into rectangular waves and from noise signals into two-bit outputs. Furthermore, the organic/inorganic hybrid transistors can be dissolved in water easily. The proposed organic/inorganic hybrid oxide transistors may have potential applications in "green" portable devices.

1. Introduction

Recently, eco-friendly "green" electronics are attracting increasing interests. It would establish low-cost routes for environmentally safe and/or biocompatible devices with energy efficient materials [1,2]. The "green" electronics will achieve unimaginable functionalities for electronics. They can be integrated into life and environment. Recently, biodegradable "green" electronics and "green" energy storages have been reported by using biodegradable materials [3–6]. Moreover, developments of flexible electronic devices with good electrical properties would enable novel applications in wearable systems [7,8], implantable electronics [9], electronic skin [10,11], flexible sensors [12], etc. Thus, fabrication of bendable devices with high flexibility and high stabilities is highly desirable. As important examples of flexible electronics, inverter circuits are essential for portable electronics. Especially, for applications in wearable electronics and portable electronics, inverter circuits with low power consumptions are highly desirable, since the capacity of portable battery is usually not high. In the family of inverter circuits, resistor loaded inverter is simple as compared to CMOS inverter and pseudo-CMOS inverter [13–16]. It can be built by connecting a resistor with a transistor in series. Conventionally, operation voltage of CMOS inverter and pseudo-CMOS inverter is high due to high operation voltage of conventional field-effect transistors [17,18]. Ionic/electronic hybrid behaviors of ionic liquid and ionic gel electrolytes in transistor configuration provide promising strategies for electrostatic modulation [19,20]. With strong electrostatic modulation behaviors of ionic liquid and ionic gel electrolytes, electrolyte gated transistors (EGTs) can operate at a low voltage of below 2V [21,22]. Therefore, introduction of ionic liquid and ionic gel electrolyte gated transistors makes it possible to drive inverters at low voltage. It could be concluded that biodegradable electrolyte gated organic/inorganic hybrid electronic devices on plastic substrates with mechanical flexibility have obvious potentials in next generation "green" portable devices.

Chitosan is a polysaccharide based biopolymer [23]. Due to non-toxicity and biodegradability, it has wide applications in biomedicine [24], food packaging [25] and cartilage tissue engineering [26,27].

* Corresponding author. Key Laboratory of Graphene Technologies and Applications of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, Zhejiang, People's Republic of China.
** Corresponding author. Key Laboratory of Graphene Technologies and Applications of Zhejiang Province, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, Zhejiang, People's Republic of China.
E-mail addresses: lqzhu@nimte.ac.cn (L.Q. Zhu), xiaohui@nimte.ac.cn (H. Xiao).

https://doi.org/10.1016/j.orgel.2018.02.005
Received 31 December 2017; Received in revised form 29 January 2018; Accepted 5 February 2018
Available online 06 February 2018
1566-1199/

Moreover, solution processed chitosan also exhibits high proton conductivities and strong electrostatic modulation behaviors [28,29]. Thus, it has potential applications in biodegradable "green" portable devices. In the present work, organic/inorganic hybrid oxide transistors were fabricated on plastic substrates by using solution processed chitosan based polysaccharide films as dielectrics. Good transistor performances were obtained. Resistor loaded inverters were built, exhibiting full-swing characteristics and high voltage gains at low operation voltages. Wave-type conversions were realized including conversions from sinusoid waves into rectangular waves and from noise signals into two-bit outputs. Furthermore, the transistors can be dissolved in water easily, indicating the potential applications in "green" devices.

2. Experimental details

Indium tin oxide (ITO) transistors gated by chitosan-based polysaccharide electrolytes were fabricated on PET substrates. Thickness (D) of the PET substrate is ~190 μm. Chitosan is commercially available. Its viscosity is 20–100 mPa s. The degree of deacetylation is ≥ 80.0%. Firstly, acetic acid activated chitosan solution was obtained with 2 wt % chitosan, 2 wt % acetic acid and 96 wt % deionized water. Acetic acid can help to dissolve chitosan in water. Chitosan will get protonized by the activation of acetic acid. Next, the chitosan solution was dip-coated on conductive PET substrate. When it is dried, a chitosan based polysaccharide film is obtained. Proton hopping is expected for the protonized chitosan films under external electrical field. We have taken cross-sectional scanning electron microscopy (SEM) characterization for the chitosan film. Its thickness was estimated to be ~12 μm (results not shown here). Then, patterned ITO films were deposited on chitosan film by sputtering ITO target in pure Ar ambient with a metal shadow mask. Ratio-frequency power, chamber pressure and Ar flow rate are set to 100 W, 0.5 Pa and 14 sccm, respectively. As schematically shown in Fig. 1 (a), an ultra-thin U-shaped ITO layer can be formed between two ITO patterns with distance of 80 μm due to the reflection of ITO nanoparticles at the mask edge [30]. Thus, an ITO transistor with bottom gate configuration is obtained. The channel length and channel width are 80 μm and 1 mm, respectively. The channel thickness can be controlled with distance between the mask and the PET substrate. Frequency dependent capacitance and phase angle of the chitosan-based polysaccharide electrolyte were characterized with an ITO/chitosan/ITO sandwich structure by using impedance analyzer (Solartron1260A). During the measurements, both DC amplitude and AC amplitude were set at 0.1 V. Electric performances of ITO transistors and resistor-loaded inverters were characterized with a semiconductor parameter analyzer (Keithley 4200). All the electric characterizations were performed at room temperature in the dark.

3. Results and discussion

Fig. 1 (b) shows frequency-dependent specific capacitance and phase angle (θ) of chitosan based electrolyte. Frequency (f) increases from 1.0 Hz to 1.0 MHz. For $f > 150$ kHz, proton migration can't follow external electric field. Electrolyte polarization corresponds to molecule polarization with $-\theta > 45°$. For 80 Hz $< f <$ 150 kHz, the electrolyte exhibits a resistive character with $-\theta < 45°$. Protons within the electrolyte will drift in response to electric field. Thus, protonic relaxation is the dominating polarization mechanism with $-\theta < 45°$. For $f < 80$ Hz, protons within the electrolyte will accumulate at chitosan/ITO electrode interface, leading to the formation of EDL layer with $-\theta > 45°$. An extremely high EDL capacitance of ~4.7 μF/cm^2 is obtained at 1 Hz. Furthermore, the effects of mechanical stress have been investigated. Fig. 1 (c) illustrates frequency-dependent specific capacitances under

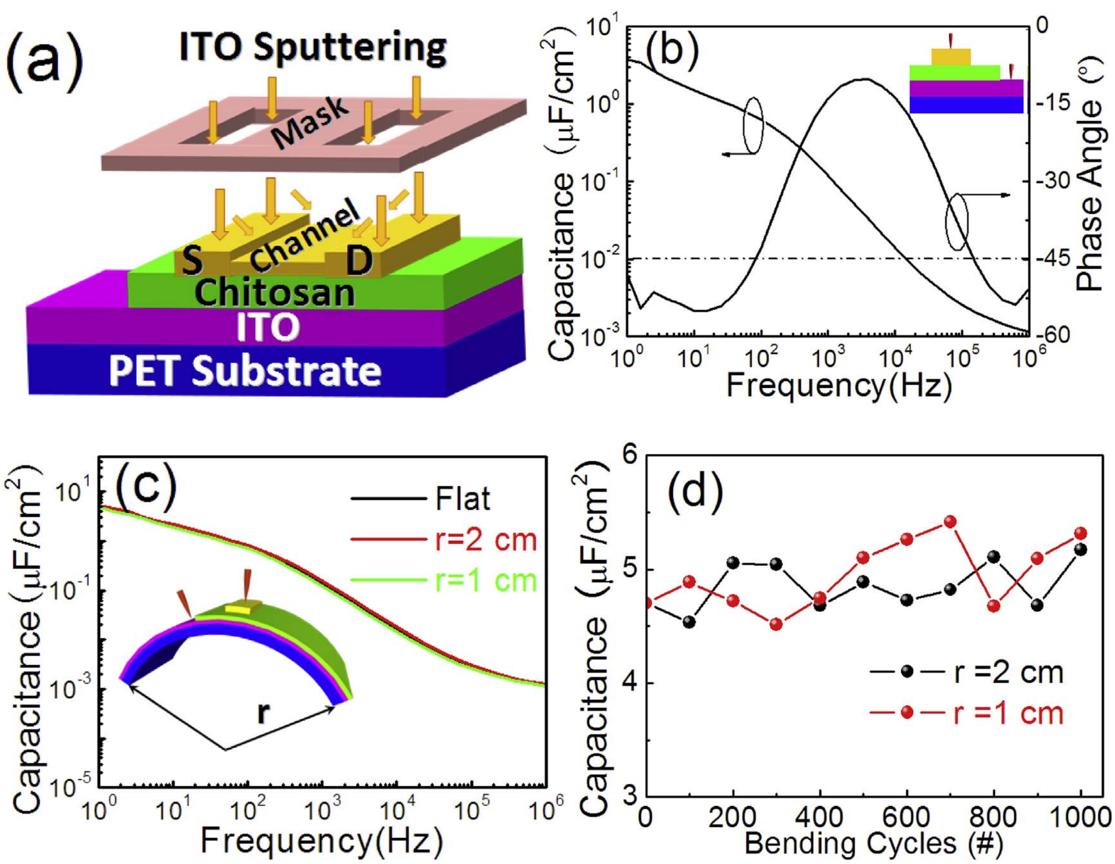

Fig. 1. (a) Schematic diagram for obtaining ITO transistor. (b) Frequency-dependent specific capacitance and phase angle (θ) of chitosan-based electrolyte film. Inset: Schematic diagram of ITO/Electrolyte/ITO capacitor. (c) Frequency-dependent specific capacitance of the electrolyte under different tensile strain. Inset: Schematic diagram for ITO/Electrolyte/ITO capacitor under tensile strain with a bending radius (r). (d) EDL capacitances as a function of bending cycles.