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Chitosan-gated low-voltage transparent indium-free aluminum-doped zinc oxide thin-film transistors

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Low-voltage transparent indium-free aluminum-doped zinc oxide (AZO) thin-film transistors (TFTs) are demonstrated by using chitosan polymer electrolyte as the gate dielectric. Chitosan with a large specific capacitance (0.4 $\mu F/cm^2$) is obtained possibly due to the strong electric-double-layer (EDL) effect through the mobile-proton hopping mechanism. Herein, low-cost indium-free AZO film is developed for replacing the traditional ITO/IZO electrodes. A simple method is developed to fabricate all of the channel and source/drain electrodes during one-step sputter process by using such a low-cost indium-free AZO film. The optimized TFTs with 30 nm AZO thickness shows the best performance with a low operation voltage of 1.5 V, a large on-off ratio of 10^5, and a field-effect mobility of 8.3 cm^2/Vs, respectively. The chitosan-gated AZO TFTs may provide a good candidate for the applications of next-generation transparent flexible low-cost portable electronics.

1. Introduction

Recently, amorphous oxide semiconductors have attracted many interests because of their intriguing properties, such as high mobility (>10 cm^2/Vs), low-temperature processing, excellent uniformity, and good transparency to visible light for the opto-electronic device applications [1–9]. Up to now, as one of basic building blocks, most of oxide-based transparent thin film transistors (TFTs) are using indium tin oxide (ITO) or indium zinc oxide (IZO) as their electrodes. However, since indium is a critical and expensive material on earth, its use in electronic devices has been threatened by its scarcity and high price [10–12]. Therefore, it is of great importance to develop alternative solutions for replacing the traditional ITO/IZO transparent conducting materials for the transparent oxide-based electronics.

On the other hand, energy consumption has turned out to be an inevitable issue especially for mobile, battery-powered applications. Thus, it is necessary to develop new gate dielectrics with a large areal capacitance. To date, the achievements of low-voltage oxide TFTs have been extensively reported in recent works, including the use of inorganic high-*k* dielectrics [13–15] or ultrathin organic self-assembled monolayer dielectrics [16–18]. In addition to above approach, an interesting alternative, named electric-double-layer (EDL), has recently been proposed as the new gate dielectrics [19–25]. Compared to traditional materials, the EDL dielectric in this kind of device acts like a nanogap capacitor (typical thickness of EDL is ~1.0 nm) [19,20], and consequently a high gate capacitance (~$\mu F/cm^2$) and a low-voltage operation (<3 V) can be easily obtained. To date, different EDL materials, such as ion liquid [19–21], ion gel [24], and polymer electrolyte [22,23,25], have been extensively reported as the gate dielectric in EDL TFTs. Among these materials, the polymer electrolyte shows a specific interest due to the solid nature, compared to the unstable liquid body in ion liquid or ion gel.

Chitosan is a cationic biopolymer derived by deacetylation of chitin [26–28]. Chitosan-based electrolyte is a potential candidate as a polymer material for different applications, such as biomedicine, biosensors, food-packaging, and fuelcells [29–31]. In this paper, we report on the low-voltage transparent indium-free aluminum-doped zinc oxide (AZO) TFTs gated with such chitosan-based proton conductors. A large specific capacitance (0.4 $\mu F/cm^2$) is obtained in chitosan-based polymer electrolyte due to the strong EDL effect, which is very favorable to the operation of low-voltage AZO TFTs. Herein, low-cost indium-free AZO film is used for replacing the traditional ITO/IZO electrodes. A simple method is further developed to fabricate all of the channel and

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source/drain electrodes during one-step sputter process by using such low-cost indium-free AZO film ("junctionless"). The as-fabricated TFTs exhibit strong AZO thickness-dependent performances. Compared with the traditional oxide TFTs, our proposed device has the following advantages: (i) The chitosan gate dielectric is a biocompatible, environment-friendly, low cost material. Most importantly, chitosan can be extensively extracted from biological waste products such as crab or shrimp shells, and thus it is regarded as the second most abundant natural polysaccharide on earth [27]. (ii) Low-cost AZO is developed as all of the source, drain, and channel layer. The indium-free material will greatly decrease the fabrication cost of oxide-based transparent TFTs [10,11]. (iii) The source, drain, and channel can be deposited by using a thin highly-doped oxide semiconductor in a one-step sputter process. The fabrication process will be simplified significantly. (iv) The device is fully transparent in visible light, and the whole device process can be performed at room temperature. Therefore, the device process is highly compatible to the fabrication of flexible transparent electronics, which is another advantage for our AZO TFTs.

2. Experimental

Our AZO TFTs are fabricated on the commercial fluorine-tin oxide (FTO) conducting glass substrates, as shown in Fig. 1. Firstly, chitosan solution (2 wt% in acetic acid) is drop-casted onto FTO-based substrates and dried in air to form a homogeneous chitosan film (thickness: ~7 μm). Then, AZO films with different thickness (15 nm, 30 nm, 60 nm, 90 nm and 120 nm) are deposited on the chitosan dielectric using radio-frequency magnetron sputtering of an AZO target (2 wt% Al_2O_3 and 98 wt% ZnO) under a power of 50 W, a working pressure of 0.5 Pa and an Ar flow rate (15 sccm). The AZO films are patterned through a nickel shadow mask with the dimension of 150 μm × 1000 μm. The capacitance-frequency measurements are performed using the Hioki IM3539 LCR Meter. The transparency measurements are based on UV–Vis spectrophotometer T9. The transfer/output characteristics of the devices are measured with a Keithley 4200 semiconductor parameter analyzer at room temperature in dark. During the electrical measurements of junctionless AZO TFTs, the signal extracting from the "drain and source regions" was performed by connecting two tungsten probes to the surface of two ends of AZO film. Every tungsten probe has a tip size of ~10 μm.

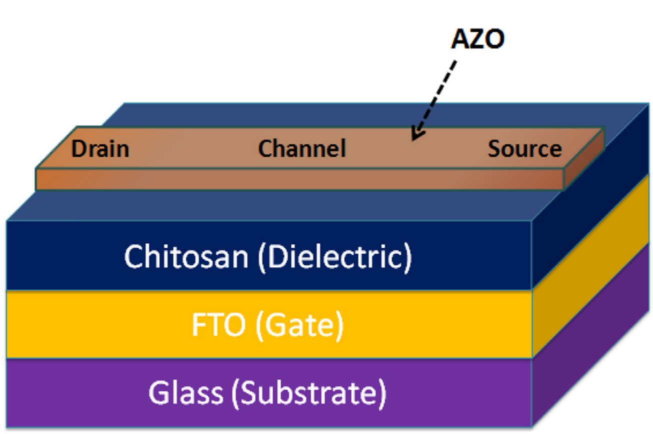

Fig. 1. The schematic diagram of chitosan-gated junctionless AZO TFTs.

3. Results and discussion

3.1. Capacitance and phase angle characteristics of chitosan film

Firstly, we characterized the solid-electrolyte behavior of chitosan by *C-f* measurements using a metal-chitosan-metal sandwich structure. The thickness of the chitosan film was found to be ~7 μm based on profiler measurements. The specific gate capacitances (C_i) of the chitosan film can be shown in Fig. 2 with the frequency ranging from 4 Hz to 100 kHz. The C_i increases with decreasing frequency and exhibits a maximum value of ~0.4 μF/cm^2 at 4 Hz. The results of phase angle can be divided into three different frequency regions by using two critical frequencies (200 Hz and 40 kHz): (1) At low frequencies ($-90°<\theta<-45°$ for $f<200$ Hz), unconventional high-capacitance behavior can be observed which is possibly due to the EDL formation at the chitosan/metal electrode interfaces [32,33]; (2) At intermediate frequencies ($-45°<\theta<0°$ for 200 Hz $<f<$ 40 kHz), the resistive behavior originates from ionic relaxation associated with dissociated protons migrating away from the chitosan biopolysaccharide chains; (3) At relatively high frequencies ($-90°<\theta<-45°$ for $f>40$ kHz), a conventional capacitive behavior is observed due to the dipolar relaxation of chitosan. The above analysis is quite consistent with the typical behavior of EDL electrolyte, and favorable for the low-voltage operation of TFTs [19–25,32–38].

3.2. Device characteristics of AZO TFTs with chitosan dielectric

The transfer curves (with a fixed V_{DS} = 1.5 V) of the organic-inorganic hybrid TFTs with different AZO thicknesses (t_{AZO}) are exhibited in Fig. 3(a). With a large AZO thicknesses (t_{AZO} = 120 nm, 90 nm), it is not surprising that the gate voltage (V_{GS}) doesn't have any modulation effect on the drain current (I_{DS}). For t_{AZO} = 60 nm, the field-effect modulation is still very weak. However, when the t_{AZO} decreases to about 30 nm, the I_{DS} is found to be strongly dependent on V_{GS}. The on-off ratio ($I_{on/off}$) and subthreshold swing(S) are found to be ~10^5 and 0.35 V/dec, respectively. When the t_{AZO} is further decreased to 15 nm, the AZO TFTs still shows a good performance with a reasonable $I_{on/off}$ of ~10^4 and a small S of 0.31 V/dec, respectively. The threshold voltage (V_{th}) of AZO TFTs can be calculated from x-axis intercept of the square root of I_{DS}-V_{GS} plot in Fig. 3(b). The V_{th} are thus extracted to be 0.2 V for t_{AZO} = 30 nm and 0.5 V for t_{AZO} = 15 nm, respectively. This t_{AZO}-dependent V_{th}

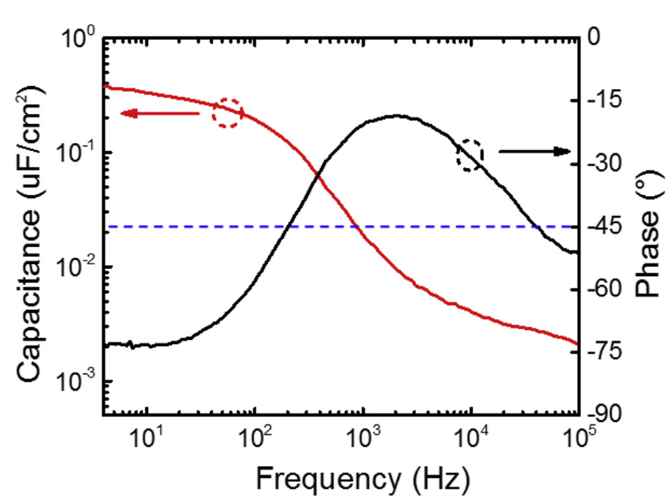

Fig. 2. Gate capacitance and phase angle of the chitosan-gated junctionless AZO TFTs with the frequency ranging from 4 Hz to 100 kHz.