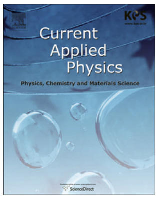
Current Applied Physics 14 (2014) S39–S43

Contents lists available at ScienceDirect

Current Applied Physics

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



Room-temperature fabrication of ultra-thin ZrO_x dielectric for high-performance InTiZnO thin-film transistors

A. Liu [a,b], G.X. Liu [a,b,*], F.K. Shan [a,b,c], H.H. Zhu [a,b,d], S. Xu [a], J.Q. Liu [b,d], B.C. Shin [c,**], W.J. Lee [c]

[a] College of Physics Science, Qingdao University, Qingdao 266071, China
[b] Lab of New Fiber Materials and Modern Textile, Growing Base for State Key Laboratory, Qingdao University, Qingdao 266071, China
[c] Electronic Ceramics Center, DongEui University, Busan 614-714, Republic of Korea
[d] College of Chemical Science and Engineering, Qingdao University, Qingdao 266071, China

ARTICLE INFO

Article history:
Received 14 August 2013
Received in revised form
9 November 2013
Accepted 29 November 2013
Available online 10 December 2013

Keywords:
Thin-film transistor
Ultra-thin ZrO_x
In–Ti–Zn–O thin film

ABSTRACT

In this letter, indium–titanium–zinc–oxide thin-film transistors with zirconium oxide (ZrO_x) gate dielectric were fabricated at room temperature. In the devices, an ultra-thin ZrO_x layer was formed as the gate dielectric by sol–gel process followed by ultraviolet (UV) irradiation. The devices can be operated under a voltage of 4 V. Enhancement mode operations with a high field-effect mobility of 48.9 cm^2/V s, a threshold voltage of 1.4 V, a subthreshold swing of 0.2 V/decade, and an on/off current ratio of 10^6 were realized. Our results demonstrate that UV-irradiated ZrO_x dielectric is a promising gate dielectric candidate for high-performance oxide devices.

1. Introduction

Amorphous metal-oxide semiconductors have emerged as potential replacements for organic and silicon materials in thin-film transistors (TFTs) electronics. The high electron mobility in amorphous state, and excellent large-area uniformity, have extended their applications to active-matrix electronics, including displays, sensor arrays and X-ray detectors [1–3]. Among these materials, InGaZnO has been studied the most extensively due to its good electrical properties. However, recent studies have pointed out their inherent problem of device instability, which deteriorates their electrical characteristics [3–6]. Light exposure and bias stressing could lead to device instabilities such as charge trapping and defect formation in the semiconductor layer or at the semiconductor–insulator interface.

To address such issues, several research groups have explored the possibility of employing alternative elements (particularly, Group IV-B elements: Ti, Zr, and Hf) in place of Ga. This incorporated element plays an important role in the suppression of carrier generation and improves the device stability by controlling oxygen vacancies. Among these candidates, TiO_2 is considered to be an attractive alternative for TFT channels because of its high mobility and similarity to ZnO in terms of the energy band gap [7–10]. Therefore, the new channel component of indium–titanium–zinc–oxide (ITZO) is expected to achieve high-performance TFTs.

Compared with organic and polymer dielectric materials, the inorganic dielectrics such as zirconium oxide (ZrO_2) [11], aluminum oxide (AlO_x) [12,13], and hafnium oxide (HfO_2) [14,15] are more suitable for low-voltage solution-processed oxide TFTs because of their large conduction band offset and excellent solvent resistance. Generally, inorganic metal-oxide formed by the sol–gel route requires an annealing step at relatively high temperature [11,12], which has prevented the incorporation of these materials with the polymer substrates used in high-performance flexible electronics. Thus, for the full realization of flexible, large-scale, solution-processed metal-oxide electronics, it is important to understand the chemistry involved in sol–gel metal-oxide formation, and to apply the knowledge to the low-temperature synthesis of dielectric films that are compatible with flexible polymer substrates and open-chamber, continuous processes.

In this work, amorphous ITZO TFT with ultra-thin ZrO_x film as the dielectric was fabricated and investigated. The whole experiment was carried out at room temperature (R.T.). The high-*k* ZrO_x thin film was fabricated by sol–gel process and densified by ultraviolet (UV) irradiation in air. Moreover, amorphous ITZO channel layers

---

* Corresponding author. College of Physics Science, Qingdao University, Qingdao 266071, China.
** Corresponding author.
E-mail addresses: gxliucn@gmail.com (G.X. Liu), shinbc@deu.ac.kr (B.C. Shin).

1567-1739/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cap.2013.11.045

deposited using radio frequency (RF) magnetron sputtering can fully satisfy the applications in large-area displays and e-papers.

2. Experiments

A bottom-gate TFT, as shown in Fig. 1, was fabricated using ZrO_x as the gate dielectric. A 50-nm thick Al layer was evaporated on the cleaned glass substrate as the gate electrode. The ZrO_x precursor solution (0.1 M) was prepared by dissolving Zr acetylacetonate $[Zr(C_5H_7O_2)_4]$ in a solvent mixed with N, N-dimethylformamide (C_3H_7NO) and ethanolamine (C_2H_7NO) at a molar ratio of 2:1. The solution was stirred at 70 °C for 3 h under ambient conditions and filtered through 0.45 μm polytetrafluoroethylene (PTFE) syringe filter before spin-coating. The precursor solution was spin-coated on Al/glass substrates at 5000 rpm for 30 s. In order to photolyze and densify the ZrO_x thin film, the sample was cured under a high-pressure mercury UV lamp in atmosphere [12,16]. The thickness of the ZrO_x thin film was controlled by repeating the coating and drying steps, one time for 5–7 nm and two times for 12–13 nm [12]. In this work, the thickness of the ZrO_x film was controlled to be 5.5 nm, as measured by ellipsometry. A 40-nm thick ITZO channel layer was then fabricated by co-sputtering a ZTO (10 mole% TiO_2-doped ZnO) target and an In_2O_3 target by using an RF magnetron sputtering at R.T. Both targets were 99.99% pure. The experimental conditions were as follows: The RF power densities for both targets were kept at 5 W/cm^2; the working pressure was 0.5 Pa; the gas flow rate for Ar and O_2 were 60 and 3 SCCM (standard cubic centimeter per minute), respectively.

Prior to the formation of source and drain electrodes, the samples were exposed to an Ar plasma treatment with Ar = 30 SCCM at 30 Watt for 60 s. Finally, 100-nm thick Al thin film was deposited by thermal evaporation to form source and drain electrodes by a shadow mask. The devices have a channel width (W) of 1000 μm and a channel length (L) of 100 μm.

The transmittances of the ZrO_x and ITZO on ZrO_x on sapphire substrates were analyzed by a UV–vis spectrophotometer (UV-2550, SHIMADZU). The surface morphologies of ZrO_x dielectric layer and ITZO film on ZrO_x were investigated by using an atomic force microscope (AFM, SPA-400, Seiko). Fourier transform infrared spectrophotometry (FT-IR, Nicolet 5700) was performed to investigate the organic bonding states of the film. The metal bonding state was investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). In order to evaluate the dielectric properties of ZrO_x thin film, the ZrO_x thin film with the structure of Al/ZrO_x/Al was investigated by using an impedance analyzer (Agilent 4294A). The electrical properties of the ZrO_x thin film and the ITZO TFT based on ZrO_x were measured by using a semiconductor parameter analyzer (Keithley 2634B) in a dark ambient environment.

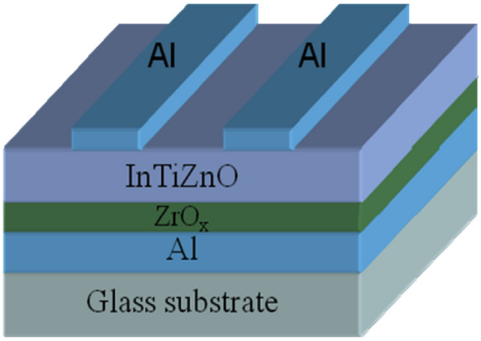


Fig. 1. Schematic structure of ITZO TFT with ZrO_x gate dielectric.

3. Results and discussion

The transmittances of the ZrO_x thin film and the ITZO on ZrO_x thin film on sapphire substrates were shown in Fig. 2. It is found that the transparency of both the ZrO_x thin film and the ITZO thin film on ZrO_x are over 80% in the visible range. This indicates the potential applications of the devices in transparent electronics.

The band gap energy of the semiconductor channel layer is an important parameter in the TFT. The electrical properties of the channel layer are sensitive to the photons with energies larger than its band gap (E_g). The band gap of the ITZO thin film was extracted by plotting $(\alpha h\nu)^2$ against the photon energy $h\nu$ and extrapolating to the energy axis. The inset of Fig. 2 shows the calculation method for the band gap energy of the ITZO thin film. The E_g determined from the obtained absorption spectrum is around 4.07 eV. This value is much larger than the photon energy of the visible light, so the ITZO TFT is insensitive to the visible light.

Fig. 3(a) and (b)show the AFM images of the UV-irradiated ZrO_x thin film and the ITZO/ZrO_x thin film, respectively. The scanning area was 2 μm × 2 μm. It is found that, after UV irradiation, the sol–gel derived ZrO_x thin film has a very smooth surface. The ZrO_x thin film has a root mean square (RMS) value of 0.40 nm and is free of pin holes. The interface roughness of the gate dielectric is one of the crucial parameters to reduce carrier scattering and obtain high filed-effect mobility. In addition, the ITZO thin film on ZrO_x fabricated by magnetron sputtering has a surface roughness of 0.82 nm. The small surface roughness is related to the amorphous nature of the ITZO thin film fabricated at R.T. and will definitely benefit the operation of the ITZO TFTs based on UV-ZrO_x dielectric.

Park et al. have ever discussed the ZrO_x formation mechanism under UV irradiation [16]. One is a relatively fast photolysis of the precursor by the UV irradiation; the other is a slower densification of the thin film due to the oxidation by a reactive oxygen species. UV irradiation at UVD (100–200 nm) and UVC (200–275 nm) in atmosphere leads to significant O_3 and active oxygen species (O^*) production. The reaction is described as:

$$O_2 \overset{UVD}{\rightarrow} O + O, \tag{1}$$

$$O_2 + O \overset{UVD}{\rightarrow} O_3, \tag{2}$$

$$O_3 \overset{UVC+UVD}{\rightarrow} O_2 + O^*. \tag{3}$$

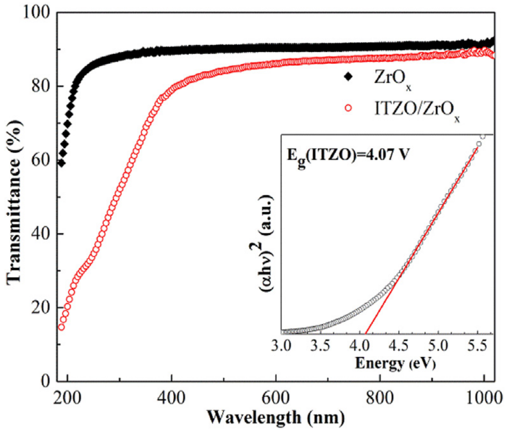


Fig. 2. Transmittances of ZrO_x thin film and ITZO/ZrO_x thin film on sapphire substrates; the inset shows the calculation method for the band gap of ITZO thin film.