High Performance Solution Processed Oxide Semiconductors and Hybrid Materials for Flexible Electronics

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ABSTRACT

Development of solution-processed channel and gate insulators is essential for large area flexible electronics. Here, we demonstrate how hybrid siloxane materials and oxide semiconductors are used in high performance fully solution-processed TFTs with mobilities >30 cm²/Vs. Our low temperature approach enables fabrication of fully solution-processed TFTs on flexible substrates.

1 Introduction

Information has become more valuable and available in the modern age especially for the potential insight and knowledge that can be extracted from it. Modern devices such as displays are crucial in the information infrastructure since displays enables viewing and interacting with information by not only being an information terminal but also an interface to interact with devices that contain/control information. Thin-film transistors (TFT) are key materials in devices which are important in current and future information infrastructure such as displays, sensors [1], memory [2], and neuromorphic devices [3]. As our society shifts towards greater connectedness between people and digital space, there is an expected surge in the number of devices that needs to be ubiquitous and fabricated in a high throughput and cost-effective manner.

Amorphous oxide semiconductors (AOS), such as amorphous InGaZnO (a-IGZO), have become the popular TFT channel material ever since a-IGZO channel was demonstrated in 2004 [4]. Its attractive combination of transparency, superb electrical properties, room temperature processability, and amorphous structure is indispensable for large area electronics. Nevertheless, most AOS devices are still fabricated by vacuum process. To address the expected growth of demand for ubiquitous devices, a paradigm shift towards alternative fabrication process such as solution process will be needed. Its widespread adoption implies that functional AOS and other TFT layers can be efficiently produced with: (1) little need for expensive equipment, (2) up to 99% material utilization for its additive processing potential, and (3) a low temperature process which is needed for ubiquitous and flexible applications in healthcare, energy, and electronic device applications. Although there have been major improvements in the performance of solution processed AOS TFTs [5, 6], there is still further work to do to improve its performance and especially stability to be comparable with vacuum process. Thus, even in many solution processed studies, only a single layer usually the channel or gate insulator (GI) is fabricated by solution process while other layers are fabricated by vacuum process as a compromise.

To truly achieve high throughput and cost-effective fabrication such as roll to roll process, it would be beneficial if all device layers are fabricated by solution process. Early variations of fully solution-processed TFTs were challenging to fabricate and had insufficient performance (mobility (μ) < 1 cm²/Vs), and poor reliability. Therefore, high temperature (>400 °C) process and exotic materials were required for acceptable performance of μ < 10 cm²/Vs [7]. Here, we demonstrate how employing solution processed hybrid materials and low temperature processing of AOS such as through light (UV, laser) and plasma process can be leveraged to develop fully solution processed TFTs with high performance (μ > 30 cm²/Vs) and improved stability.

2 Experiment

2.1 Hybrid PSX material

Polysiloxane (PSX) materials (see Fig 1(a) for the structure) including polysilsesquioxane are hybrid inorganic-organic materials with an inorganic Si-O backbone and organic functional groups [8] and have been extensively used in various device applications. Its structure allows for flexibility in design so that additional functionalities can be achieved. For instance, (1) the functional groups can be varied in PSX so that it has improved mechanical properties or fabricated at lower temperatures; (2) PSX can be fluorinated to enhance TFT performance; and (3) nanoparticles with high dielectric constant (k) can be incorporated into PSX to form nanocomposite films that retain high k-value at low fabrication temperature.

Here, PSX is used as either the GI of a-IGZO TFT (Fig 1(a)) [9] or passivation of solution processed a-InZnO (a-IZO) TFT (Fig 1(b)) [10]. Both TFTs had a bottom gate top contact structure with nominal channel thickness of 70 nm. As a GI, $BaTiO_x$ (BTO) nanoparticles (NP) were incorporated into PSX at a BTO/PSX ratio of 1.4/1.0. Additional fluorinated BTO/PSX precursors were also prepared. Prior to the spin-coating of the BTO/PSX GI on the Si substrate (gate), the native oxide was removed by BHF etching. As a passivation material, fluorinated PSX was deposited either via spin-coating or spray-pyrolysis to from a 450 nm passivation layer. The precursor used for spin-coating and spray-coating had a 30% and 5% solid content, respectively.

2.2 High performance fully solution processed AOS TFTs

Development of a fully solution processed TFT is indispensable for cost-effective high throughput device fabrication. Through the combination of high performance hybrid materials and AOS subjected to a low temperature process, it is possible to develop fully solution processed TFTs even on flexible substrates. To fabricate the fully solution processed TFT, an a-IZO layer was consecutively spin-coated to form a 70 nm film. Fluorinated PSX was then spin-coated as the GI. Using the same fabrication conditions as the first 70 nm a-IZO layer, another 70 nm a-IZO layer was then spin-coated as the third layer. Photolithography and etching were then performed to create a self-aligned structure (see Fig 4(b)). To form the gate, source, and drain regions, the structure was subjected to either photo-assisted process such as UV and laser irradiation or plasma treatment. These low temperature processes transformed the exposed a-IZO regions into conductive source/drain, and gate regions (see Fig 4(c)).

3 Results and Discussions

A great advantage of utilizing hybrid PSX GI is its high tunability. In Fig. 2, we demonstrate how the addition of high-*k* BTO NP and subsequent fluorination led to high performance a-IGZO TFT with low turn-on voltage while maintaining a low off-current. The addition of high-*k* BTO NP at a BTO/PSX ratio of 1.4/1.0 increased the *k*-value to 8.9 from ~3.0. However, as shown in Fig 2(a), the off-current and leakage current (I_g) increased to 10^{-10} A and 10^{-7} A, respectively. Through incorporation of fluorine, we have managed to address the high off-current and I_g present in $BTO_{1.4}PSX_{1.0}$ which has high BTO ratio.

Both a-IGZO TFTs with non-fluorinated $BTO_{1.4}PSX_{1.0}$ GI and fluorinated $BTO_{1.4}PSX_{1.0}$ GI had similar μ of 23.81 cm^2/Vs [12] and 21.86 cm^2/Vs, respectively. The difference in both Ig and off-current, however, is significant as the fluorinated $BTO_{1.4}PSX_{1.0}$ GI had a drastically reduced off-current and I_g of 10^{-12} A and 10^{-9} A, respectively.

Aside from GI applications, fluorinated PSX can be effectively used as a passivation material. Fig. 3 demonstrates the bias stress stability improvement both spin-coated (SC) and spray-coated (SP) fluorinated PSX passivation impart to solution processed a-IZO TFT subjected to positive bias stress (PBS, V_g = 20 V) for 10,000 s. All TFTs showed positive parallel threshold voltage shifts (ΔV_{th}) which imply that the degradation mechanism is mainly electron trapping at either the channel/GI interface, channel bulk, or back-channel surface or interface with the passivation with minimal defect creation. The large ΔV_{th} of 2.4 V in unpassivated a-IZO TFT is expected and well-known to be due to interaction of the back-channel with ambient gases and moisture.

In the case of the passivated a-IZO TFTs and considering that all samples had identical gate insulator (thermal SiO_2), the improvement in PBS stability is primarily due to the inclusion of the fluorinated PSX. The addition of fluorine is particularly helpful since it can improve the passivation film density, potentially increase carrier concentration, and passivate oxygen vacancy defects. Although both SC and SP fluorinated PSX passivation had almost similar PBS results, the a-IZO TFTs with SP fluorinated PSX passivation had better stability against both negative bias stress and humidity stress (data not shown). We found that better stability is observed with the SP variant due to its better film quality as shown by its higher hydrophobicity and superior film density via higher crosslinking density [10].

The use of hybrid PSX materials when combined with low temperature processing of AOS can enable the development of fully solution processed TFTs. Fig 4(b) shows the structure of the fully solution processed TFT before the transformation of selective AOS regions into conductors either through UV, laser irradiation, or plasma. Without these processes, the selective regions have insufficient conductivity to act as source, drain, and gate electrodes. As a result, the fully solution processed TFT exhibited no transfer characteristics (data not shown) before the conversion process. After subjecting the device to a combination of UV and excimer laser annealing (ELA), high performance fully solution processed TFTs with μ of up to 39 cm^2/Vs can be achieved [11]. We calculated the penetration depth of UV (254 nm) and ELA (248 nm) to be ~80 nm and ~81 nm, respectively. Thus, a single layer of a-IZO can act as both channel and source/drain electrode and the photo-induced conductivity enhancement is not only limited to the a-IZO surface but affects the entire a-IZO bulk. Similar high performance fully solution processed a-IZO TFT can be achieved through continuous wave (CW) laser and plasma treatment. The key mechanism to the high performance is the photo-induced activation of the AOS. We found that both UV and ELA can reduce the a-IZO sheet resistance which decreases the resistivity of a-IZO by up to 2 orders of magnitude to ~10^{-4} Ω·cm.

Fig. 5 shows the simulation of laser-induced heating on the fully solution processed TFT after ELA. The results indicate that high temperatures are localized at upper layers and temperatures of <50 °C are induced at the substrate. Considering that the maximum process temperature of the UV treatment is 115 °C and that the substrate is only subjected to <100 °C after ELA, we fabricated fully solution processed TFTs on flexible substrates. Fig 6 shows that we have successfully fabricated fully solution-processed TFTs on flexible substrates. With further optimization, we think that flexible high performance fully solution processed TFTs will be achieved.

4 Conclusion

In this report, we demonstrate how the tunability of hybrid materials can be used to create high-*k* GI and high-quality passivation material for AOS TFTs. In addition, we show that combining these hybrid materials with low temperature processing of AOS can enable the development of high performance fully solution processed TFTs with μ > 30 cm^2/Vs. The low temperature process (<115 °C) that we use to functionalize our fully solution processed TFTs is also indispensable in developing flexible fully solution processed TFTs. These results exhibit the large promise of solution-processed hybrid films and low temperature processing of solution-processed AOS in developing cost-effective and high throughput fabrication of high performance fully solution-processed devices on flexible substrates.

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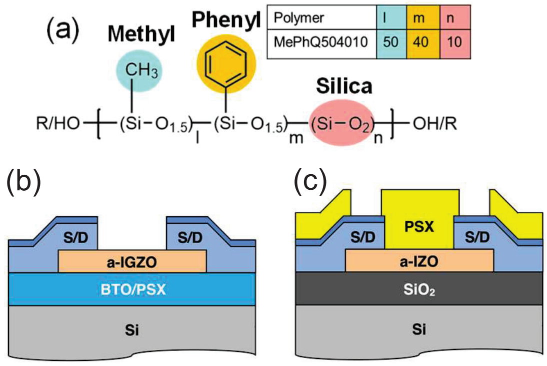

Fig. 1 (a) PSX structure (b) a-IGZO TFT with BTO/PSX gate insulator (c) a-IZO TFT with PSX passivation

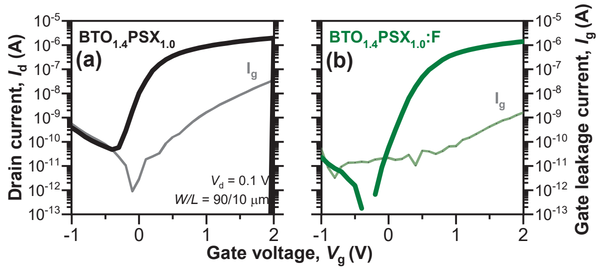

Fig. 2 Transfer characteristics and gate leakage current of a-IGZO TFT with (a) $BTO_{1.4}PSX_{1.0}$ and (b) fluorinated $BTO_{1.0}PSX_{1.0}$

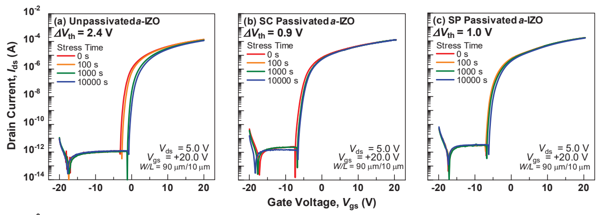

Fig. 3 Evolution of transfer characteristics of solution processed a-IZO TFT with (a) no passivation (b) spin-coated and (c) spray-coated Fluorinated PSX after PBS stress of 10000 s

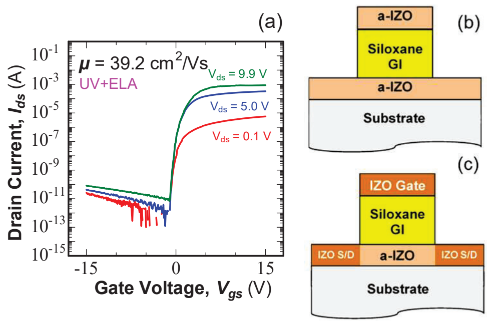

Fig. 4 (a) Transfer characteristics of fully solution-processed a-IZO TFT. Structure of fully-solution processed TFT (b) before and (c) after electrode activation with either UV, laser irradiation, or plasma process

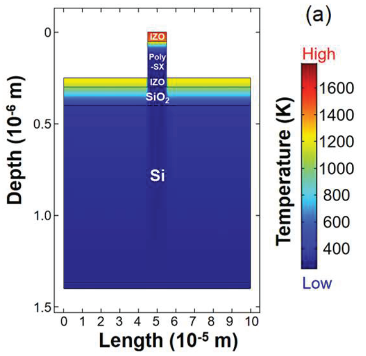

Fig. 5 2D multiphysics simulation of laser-induced heating of fully-solution processed TFT.

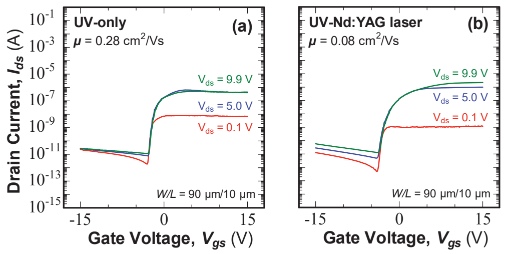

Fig. 6 Transfer characteristics of fully solution-processed a-IZO TFT on flexible substrates