# Thin film transistors with printed semiconductive oxide channel and silver source-drain electrodes

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## ABSTRACT

Ink-jet printed silver was used as source/drain electrodes to construct thin film transistors (TFTs) with solution-processed zinc indium tin oxide (ZITO) channel layer annealed at 400 $^{o}$C. The thermal stability of printed silver electrodes was investigated. A electric conductive degradation of silver tracks was found after annealing at 300 $^{o}$C in air. To understand and optimize the transistor performance, ZITO film thickness and compositional influence on device performance were invesigated. Thin film transistors were fabricated through ink-jet printing semiconductive oxide channel and silver source/drain electrodes. The ZITO TFTs with printed semiconductive oxide channel and silver source/drain electrodes have on/off ratios of more than $10^4$ and saturation mobility of ~0.10 $cm^2/V\cdot s$.

***Keywords***: printed electronics, TFTs, TAOS, conductive ink

## 1 INTRODUCTION

Printing techniques have many advantages of low-cost, high throughput, large area *etc*. Printed thin-film field-effect transistors have attracted considerable attention because of their extensive use in large-area and flexible electronics applications. A field-effect transistors is composed of semiconductive channel, source/drain electrodes, gate dielectric layer and a gate electrode. For the semiconductive channel layer, amorphous oxide such as zinc oxide (ZnO), zinc-indium oxide (ZIO), zinc-tin oxide (ZTO), zinc-indium-tin oxide (ZITO), zinc indium gallium oxide (ZIGO), etc, are promising candidate materials, as they are of high mobility, high stability, low processing temperature, and most importantly, printable [1].

Recently, thin film transistors with solution processed and printed amorphous oxides have been by far investigated [2-6]. Despite impressive progress, in most of them, only the oxide semiconductor layers were doposited by printing and the electrodes were still made by conventional vacuum deposition of metals or ITO [2-5]. However, in order to make all-printed thin-film transistors, the key issue such as the interfacing effect between printed electrodes and printed semiconductive channel layer has to be solved [7]. Moon *et. al.* reported a thin film transistor device with spin-coating semiconductor and printed zinc indium oxide (ZIO) electrode [5]. However, the ZIO electrodes must be annealed at high temperature of 600 $^{o}$C, which is even higher than annealed temperature of oxide semiconductor layer. Printable Ag ink have been extensively researched and are commerially available [8]. Moreover, silver tracks could be activated at lower temperature.

In this study, ink-jet printed silver source/drain electrodes were used in printed or spin-coating ZITO TFTs. Thermal behavior of printed silver electrodes, the dependence of device performance on film stoichiometry and thickness was studied. Thin film transistors with printed semiconductive oxide channel and silver source/drain electrodes were demonstrated.

## 2 EXPERIMENTAL METHODS

All reagent were purchased from Sinopharm Chemical Reagent. The inkjet-printable precursor ink for the ZITO semiconductor layer was synthesized by dissolving zinc acetate dihydrate ($Zn(CH_3COO)_2\cdot 2H_2O$, 99%), indium(III) choloride ($InCl_3$, 99%) and tin(IV) chloride pentahydrate ($SnCl_4\cdot 5H_2O$, 99%) in 2-methoxyethanol (99%) with special molar ratios. The overall metal cation concentration for spin-coating and ink-jet printing was 0.5 M and 0.2 M, repsectively. Ethanolamine was added to the precursor solution as a stabilizing agent to improve solubility of the precursor salts. Solution was filtered through a 0.22 μm membrane prior to spin-coating and ink-jet printing semiconductive layer.

Heavily n-doped Si wafer with a thermally grown 300 nm thick $SiO_2$ layer was used as dielectric layer/gate electrode. The $SiO_2/n^+$-Si substrate was ultrasonic cleaned with acetone, ethanol, and deionized water in turn, followed by drying it in stream of clean dry nitrogen gas, before transistor fabrication. Semiconductor percursor layers were deposited by spin-coating or inkjet-printing. Both ZITO and silver inkjet-printing processes were performed using Dimatix material printer DMP-2831 with nozzel of 20 μm diameter. When printing ZITO channel and silver electrodes, temperatures of substrates were room temperature and 60 $^{o}$C, respectively. The as-deposited ZITO precursor films were dried at 200 $^{o}$C for 10 min to evaporate solvent and then annealed at 400 $^{o}$C for 1h in air for activating semiconductor channel. The Ag source/drain electrodes were ink-jet printed on top of the ZITO layer on $SiO_2/n^+$-Si, then activated by annealing at 200 $^{o}$C for 30 min in air. The channel width (W) and length (L) were 1 mm and 200 μm, respectively. To understand the dependence of device performances on film thickness and metal content in semiconductor ink, the transistors were fabricated by spin-coating of semiconductive layer. Different layer thicknesses were obtained by spin coating sol-gel of ZITO on substrates through controlling spin speed and duration. Transistors with ca. 50, 90, 120 nm thick ZITO layer were investigated. Printed ZITO layer thickness and uniformity were controled by waveform, volatility of solution and drop space. The film thicknesses were determined by Spectroscopic Ellipsometer (M-2000DI, J.A.Woollam). The electrical characteristics of the field-effect transistors were measured using Keithley 4200 semiconductor parameter analyzer in ambient condition.

## 3 RESULTS AND DISCUSSION

### 3.1 Thermal stability of printed silver electrode

If printed silver was used as one part of devices or circuits, it must undergo thermal treatments which are necessary to activate other functional layers, such as annealing semiconductive oxide layer in air at 200-600 °C. In addition, electric conductivity of printed silver wire depends on thermal treatment, which influences silver particles sintering and removal of organic additive. Thermal stability of printed silver wires with width of 0.3 mm and length of 30 mm were studied. After annealing at 200 °C for 30min in air, 1-4 times printed silver wires all have good conductive, as presented in Table 1. Further annealing at 300 °C for 1 hour, 1-2 times printing silver wires lost their electric conductivity, and reduction of conductivity was also found in 3 or more times printed silver wires. Sintered silver could not be oxidated at 300 °C in air according to thermodynamics. Such conductivity degradation was due to formation of crack in silver wires. The crack greatly depends on the amount and sort of organic additive in silver ink, because removal of organic additive will cause shrinkage of the silver lines [8]. To void device failure due to such degradation, silver electrods must be deposited after oxide deposition. Therefore, a bottom-gate/top-contact configuration was utilized, as shown in Fig. 1.

| Printing Times | only annealing at 200 °C (Unit: Ω) | further annealing at 300 °C (Unit: Ω) |
|---|---|---|
| 1 | 280.9 | non-conductor |
| 2 | 83.3 | non-conductor |
| 3 | 40.8 | 2898.6 |
| 4 | 36.2 | 1607.7 |

Table 1: Resistances of silver wires fixed 0.3mm width and 3mm length obtained through printing for 1-4 times: only annealing at 200 °C in air for 30 min and further heating in air at 300 °C for 1 hour.

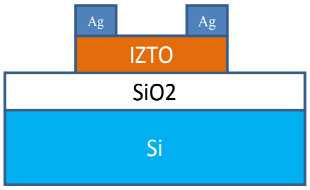

Figure 1: Schematic diagram of ZITO TFT structure. It has bottom-gate and top-contact device configuration.

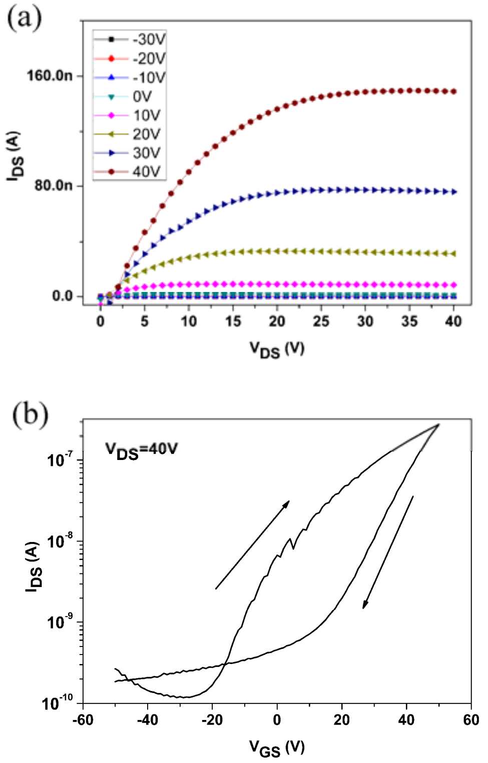

Figure 2: Output (a) and transfer (b) characteristics of thin film transistor with 50 nm thickness ZITO (Zn:In:Sn=1:4:4) layer.

### 3.2 TFTs performance dependence on semiconductor layer thickness

Figure 2-3 showed the output and transfer plots of ZITO (Zn:In:Sn=1:4:4) TFTs with ca. 50 and 90 nm ZITO layer, respectively. Both ZITO TFTs with 50 and 90 nm thickness channel layer have demonstrated transistors characteristcs. The off-current and on-current increased from $10^{-10}$ to $10^{-8}$ A and $10^{-7}$ to $10^{-6}$ A when increasing the ZITO layer thickness from 50nm to 90 nm, respectively. When increasing ZITO thickness to 120 nm or more, the ZITO TFTs have too high off-current of $10^{-4}$A resulting in the lost of transistors characteristics. Although ZITO TFTs with thickness of 50 nm have slightly higher on/off ratio ($10^3$) than 90 nm transistor ($10^2$ of ratio), thinner layer TFTs have larger hysteresis than thicker layer TFTs. Based on the on/off ratio and hysteresis, the optimal film thickness for ZITO channel layer is approximately 90 nm.

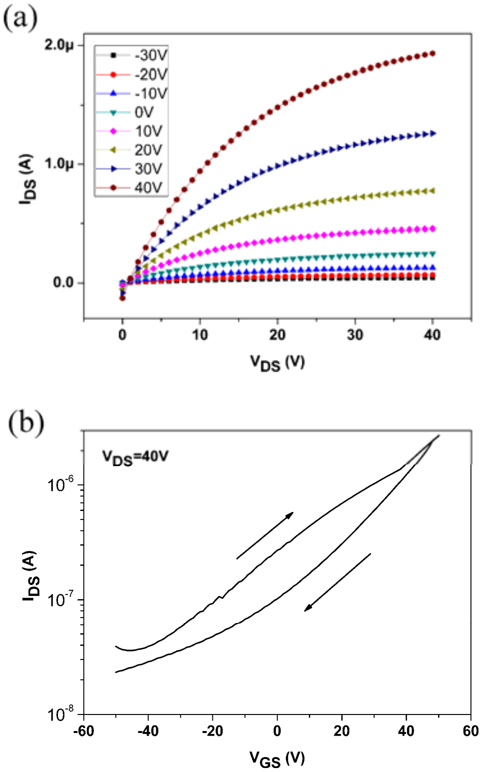

Figure 3: Output (a) and transfer (b) characteristics of thin film transistor with 90 nm thickness ZITO (Zn:In:Sn=1:4:4) layer.

Previous studies have reported similar observations in which the thicknesses of solution-processed oxide semiconductors play an important role in devices performances [4]. There are more free charge carriers exist after filling the trap sites in thicker film, so the off-current increases drastically. The dependence of TFTs' electrical properties on active layer thickness could be explained on the basis of free carrier density and interface scattering. [9] . Higher number of free carriers in the bulk of the thicker films results in an easier accumulation of charges at the interface between semiconductor and dielectric, which is consistent with the observed increase in the on-current for those films [10]

## 3.3 TFT performance dependence on the composition ratio of semiconductor oxide ink

Besides ZITO (Zn:In:Sn=1:4:4), Zn:In:Sn=1:1:1 and Zn:In:Sn=2:1:1 were also used as semiconductor layer of TFTs. When ZITO (Zn:In:Sn=2:1:1) was used as channel layer, the devices did not show transistor characteristics and drain-source current always was lower than $10^{-9}$ even changing the gate voltage from -50 V to 50 V. It had been found that the increase in the $Zn^{2+}$ content of ZITO induce a significant mobility decline [11]. ZITO (Zn:In:Sn=1:1:1) have the similar TFTs characteristics as ZITO (Zn:In:Sn=1:4:4), slightly lower on/off ratio and larger hysteresis.

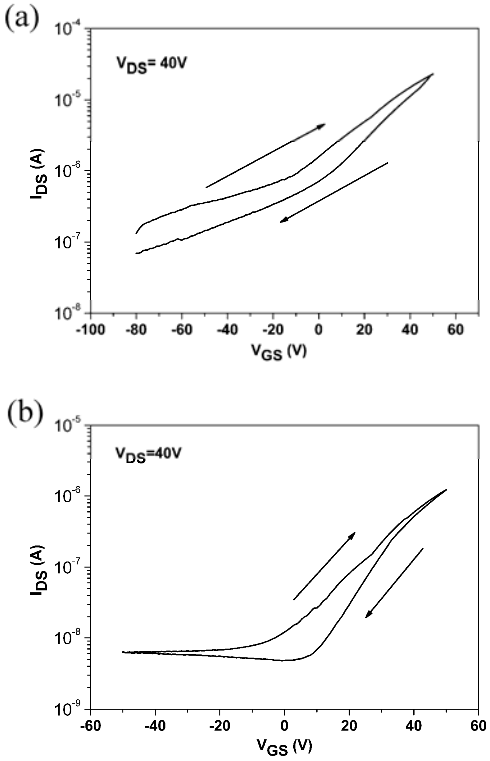

Figure 4: transfer characteristics of thin film transistor with 90 (a) and 50 nm (b) thickness ZITO (Zn:In:Sn=1:1:1) layer.

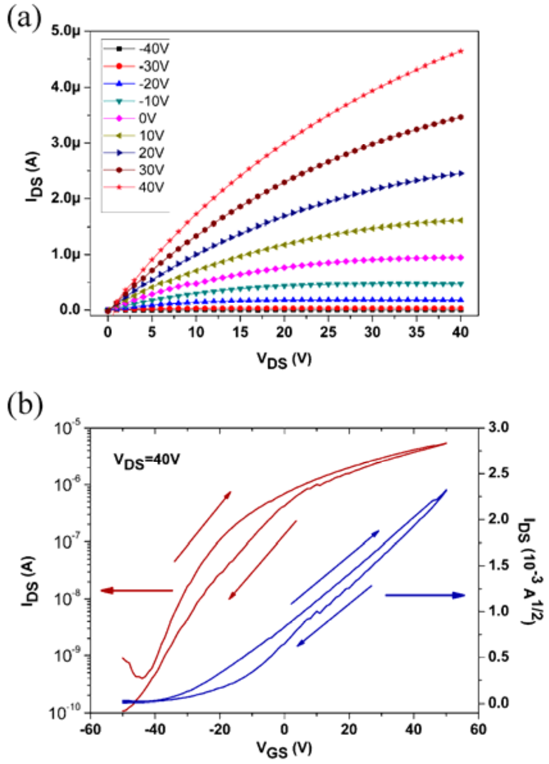

Figure 5: Output (a) and transfer (b) characteristics of thin film transistor with ink-jet printed 100 nm thickness ZITO

(Zn:In:Sn=1:4:4) layer and ink-jet printed Ag source/drain electrodes.

### 3.4 Printed ZITO transistor performance

Figure 5 shows the transistor characteristics with printed silver source/drain electrodes and printed ZITO (Zn:In:Sn=1:4:4) semiconductor layer. It is surprising that the printed ZITO (Zn:In:Sn=1:4:4) transistors with ca. 100 nm thick channel layer have better characteristics than those with spin-coated semiconductor layers. The transistors have more than $10^4$ on/off ratio due to lower off-current. The lower off-current may be attributed to reduced peripheral leakage. On the other hand, ink-jet deposited film should have different microstructure and morphology from spin coated film because of different volatility of solvent and the way the film is formed. The transistor mobility $\mu_{eff}$ was extracted in the saturated operation regime from the transfer curve using formule $I_D=\mu_{eff}\ C_iW(V_G-V_T)^2/2L$. The ZITO TFTs with printed semiconductive oxide channel and silver source/drain electrodes have saturation mobility of ~0.10 $cm^2/V\cdot s$.

## 4 CONCLUSIONS

Thin film transistors with printed semiconductive oxide channel and silver source/drain electrodes were fabricated using ink-jet printing process, where zinc indium tin oxide (ZITO) layer was annealed at 400 $^oC$. The optimized ZITO metal ratio was Zn:In:Sn=1:4:4 and optimized thickness is about 90nm in this study. TFTs with printed semiconductive oxide channel and silver source/drain electrodes have on/off ratios of more than $10^4$ and saturation mobility of ~0.10 $cm^2/V\cdot s$. A degradation of electric conductivity in the silver tracks was found after annealing at 300 $^oC$ in air.

## 5 ACKNOWLEDGMENTS

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