Direct Writing of Semiconducting Oxide Layer Using Ink-Jet Printing

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Abstract

Zinc tin oxide (ZTO) sol-gel solution was synthesized for ink-jet printable semiconducting ink. Bottom-contact type TFT was produced by printing the ZTO layer between the source and drain electrodes. The transistor involving the ink-jet printed ZTO had the mobility ~ 0.01 $cm^2V^{-1}s^{-1}$. We demonstrated the direct-writing of semiconducting oxide for solution processed TFT fabrication.

1. Introduction

Traditionally, photolithography technology has been widely used for patterning in the thin film transistors (TFTs). However, there is currently significant interest in realizing high performance TFTs based on solution processable semiconducting materials for applications requiring low-cost manufacturing for large area display devices.[1-3] Ink-jet printing technique of functional materials is one of the alternative technique ver high-cost photolithography.[4] Ink-jet printing requires low viscosity liquid phase materials, i.e, inks, to be printed through a nozzle, from which the semiconducting layer forms after drying. For such semiconducting inks, solution processable organic semiconductors had been used such as poly[5.5'-bis(3-dodecyl-2-thienyl)-2.2'-bithiophene] (PQT-12), poly(3-hexylthiophene) (P3HT) or α,ω-dihexyl-quaterthiophene (DH4T).[5-6] However, their electrical properties are unstable in ambient air. In this regard, inorganic inks such as silicon and zinc indium oxides have been reported recently.[7] Especially, several multi-cation oxides – zinc tin oxide, zinc indium oxide, and indium gallium zinc oxide – have been shown to provide improved performance, as compared to organic semiconductor and amorphous Si.[8-9] In this study, we developed a semiconducting ink which contains the precursor of zinc tin oxide. The ink was stable so that the printing can be performed in air. The printing conditions such as pulse frequency, pulse amplitude, and xy-stage moving velocity were optimized to achieve smooth semiconducting layer with high resolution. Thin film transistor were fabricated with this semiconducting layer and I-V measurement was performed.

2. Experimental

The ZTO ink was synthesized from zinc acetate dihydrate ($Zn(CH_3COO)_2 \cdot 2H_2O$, Aldrich) and tin acetate ($Sn(CH_3COO)_2$, Aldrich) in 2-methoxyethanol (Aldrich), by sol-gel synthesis method. The precursor solution was stirred at elevated temperature until the precursor completely dissolved and the solution became clear. The sol stabilizers were added into the solution. The solution was stirred for 12 hour at room temperature. The viscosity of the inks was 17.8 mPa·s at a shear rate of 50 s^{-1}, which was measured by a cone and plate viscometer (DV-III+, Brookfield Engineering).

Bottom contact type transistors involving the solution-processed semiconductor were fabricated on ITO patterned heavily doped silicon substrate with 200 nm-thick SiO_2 dielectric layer. The ITO electrodes was deposited by sputtering and patterned by photo lithography. The channel length (L) and width (W) were 50 ㎛ and 300 ㎛, respectively (W/L ratio ~ 6). The ZTO semiconducting ink was printed on the ITO patterned SiO_2/Si substrate by an ink-jet printer. The printer set-up consists of a drop-on-demand (DOD) piezoelectric ink-jet nozzle manufactured by Microfab Technologies, Inc. (Plano, TX) with a 50 ㎛ orifice. The ZTO deposited substrate was annealed for 4 hour at 500℃ to eliminate the solvent and other residue except for zinc tin oxide. I-V measurements were performed in air using an Agilent 5263A sourcemeasure unit. Microstructures of the ZTO films were observed by scanning electron microscopy (JSM 6700F, JEOL) and confocal laser scanning microscope (CLSM 5 Pascal, Carl Zeiss).

3. Results and discussion

Figure 1 shows two- and three-dimensional images of ink-jet printed ZTO dots on a wafer, obtained by a confocal laser scanning microscope (CLSM 5 Pascal, Carl Zeiss). The ejected droplet from nozzle has a diameter of about 59 ㎛ and the velocity of 1.5 m/s. A single droplet of solvent placed on the substrate evaporates under ambient conditions, resulting in spherical deposits of silver nanoparticles with dot sizes in a range of 300 ~ 350 nm. When the ZTO ink was deposited on substrate by spin-coating, the thickness was 50 ~ 60 nm and the surface was flatness. In contrast, the surface of ink-jet printed ZTO layer is rather rough and uneven.

Figure 2 shows cross-sectional SEM of ink-jet printed ZTO layer. The ZTO film adheres well to underlying SiO_2 substrate without noticeable crack and delamination. Film thickness in the middle part of the printed film is ~210 nm.

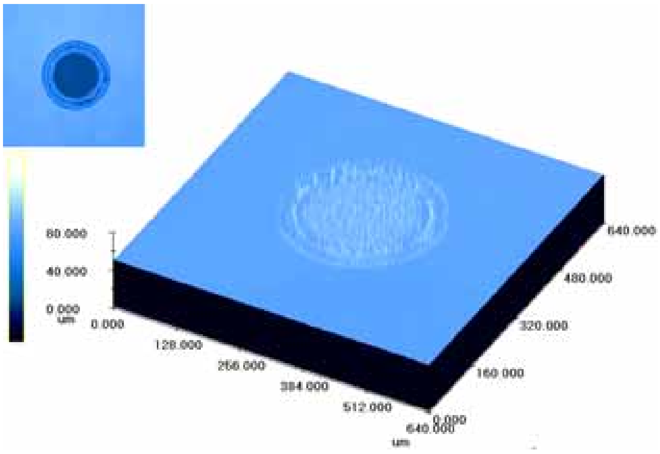

Fig. 1. Confocal image of ink-jet printed single deposition pattern of ZTO films.

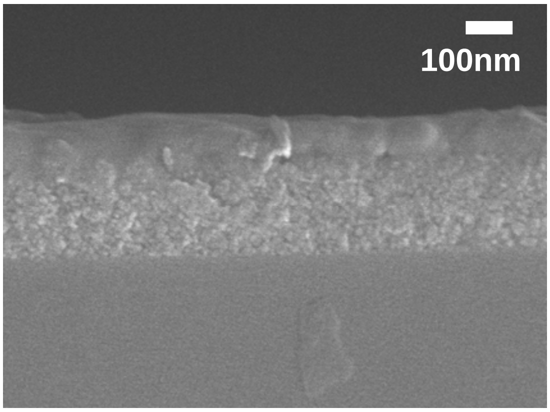

Fig. 2. SEM micrographs of cross-section of ink-jet printed ZTO semiconducting layer.

Figure 3(a) and 3(b) are transfer and output characteristics of TFT with ink-jet printed ZTO layer which contains 25 mol% Sn. Inset shows the ink-printed ZTO between the source and the drain electrode. The mobility in the saturation regime was 0.01 $cm^2V^{-1}s^{-1}$ and on/off current ratio was 10^5.

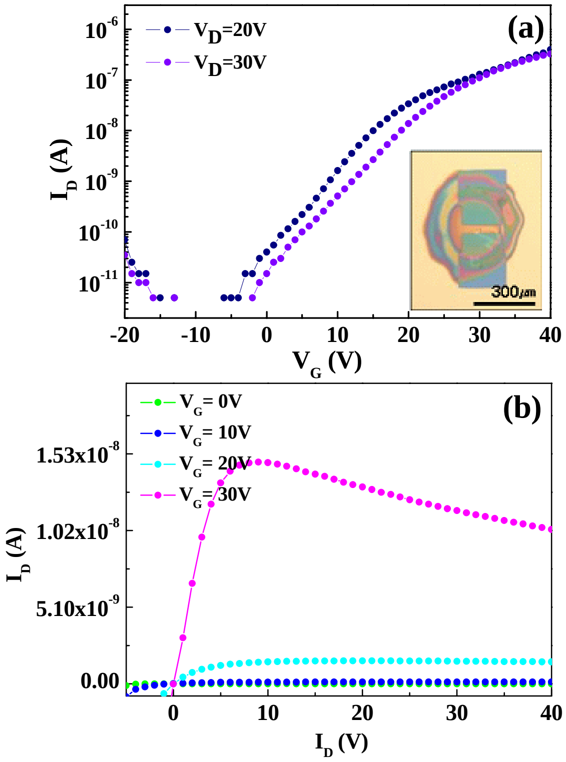

Fig. 3. Transfer and output characteristics of ink-jet printed ZTO semiconductor-based transistor..

Turn-on voltage of the transistor was determined to be -3V at gate bias 30V. Turn-on voltage (V_{on}) is simply identified as the gate voltage at which the drain current increase begins in the transfer curve. The term 'V_{on}' is used instead of threshold voltage (V_{th}) herein because V_{on} could describe switching behavior directly.

In figure 3(a), the existence of a break in the transfer curve near -10V is because of much lower off-current detection beyond instrumental limitation in our measurement system. When the semiconductor is patterned, the off current of the device becomes lower than spin-coated film. Although the mobility of ZTO is still much lower than the vacuum deposited oxide semiconductors, it is meaningful that the oxide semiconductor could be fabricated by ink-jet printing. Further improvement of the device performance is currently underway.

4. Summary

We developed a semiconducting ZTO ink and achieved a technique by which the well-defined pattern is produced by ink-jet printing. Thin film transistor using this ZTO layer was fabricated. It was observed that the mobility was 0.01 $cm^2V^{-1}s^{-1}$ and on/off current ratio was 10^5. This offers the potential of replacing photolithography which involves several complex processing steps.

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