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Solution-Processed Zinc-Tin-Oxide Thin-Film Transistor by Electrohydrodynamic Spray

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Solution-processed zinc-tin-oxide film was coated by electrohydrodynamic (EHD) jet. By using EHD spray technique, zinc-tin-oxide (ZTO) TFT was prepared and characterized for the first time. The optimized process parameters were as follows: an electrical voltage of 3 KV to apply nozzle, a solution pursing of 0.032 μl per sec, a distance of 45 mm between nozzle and substrate for 30 sec with a 0.3 M of ZTO solution. The electrical properties were obtained as follows; a mobility of 2.0 cm^2/Vs, a current ratio Ion/Ioff of 10^5, a threshold voltage of −10 V, a subthreshold slope of 1.74 V/dec. Based on this result, more in-depth research should be performed in this specific area for further development and electronic applications.

Keywords: zinc-tin oxide TFT, EHD jet, spray coating, solution-process

1. INTRODUCTION

Amorphous silicon thin film transistors (*a*-Si TFTs) are widely used for consumer electronics and have been demonstrated to be useful for use in solar cells and flexible displays. Organic thin film transistors are of interest for applications in low-cost electronic devices such as radio-frequency identification tags, flexible displays, memory and sensors. However, the applications of these devices are limited by their low mobility and light/moisture sensitivity due to intrinsic material properties.

Transparent conducting oxide (TCO) and oxide semiconductor films have been used in many applications as transparent electrode materials for flat panel display devices, touch panels, and solar cells.[1] Among them, the amorphous multi-components oxide IGZO was intensively studied for organic light emitting diodes (OLED) and solar cell applications. IZO thin films also show good electrical properties. However, those materials have major drawbacks due to indium's supply and expensive price. ZTO may be an interesting material for future TCOs and for oxide semiconductor development because of its wide band gap, low cost and nontoxicity. Until now most of oxide semiconductors for TFT application have been prepared by vacuum deposition processes such as sputter, PLD and ALD.[2-4]

In order to achieve flexible display, low temperature process of solution processed oxide thin-film transistor (TFT) is highly demanded. Displays fabricated with plastic substrate have the advantage of flexible, thin, light, and non-fragile characteristics with printing process, and show the high possibility of low cost and large area. Printing processes applied to TFT for display are mostly ink-jet, micro-contact, and roll printing with high speed through put process, which can dramatically reduce the process cost.

Recently spray coating and spray pyrolysis were reported to as alternative printing techniques for electronic devices. Anthopoulos *et al.* published spray pyrolysis to prepare zinc oxide TFT, exhibited n-channel characteristic with electron mobility of 10 - 22 cm^2/Vs. High performance ZnO TFT and circuits were fabricated by spray pyrolysis by applying self-assembled monolayer dielectric to obtain low voltage operation.[5] There was an electrohydrodynamic (EHD) jet printing. Rogers *et al.* reported high resolution patterning under submicron, metal interconnect and electrodes for the potential application of electronics.[6] The advantage of EHD jet printing over conventional ink-jet technique lies high resolution.

However, there was no report regarding EHD spray method for preparing TFT yet. We tried to fabricate EHD sprayed solution-processed oxide TFT for the first time.

2. EXPERIMENTAL

The bottom-gate and top-contact solution processed ZTO TFT was prepared. As an active layer, zinc acetate dehydrate and tin chloride were mixed in 2-ethoxyethanol to form a sol-gel solution mixture, 0.3 M with the same molar ratio of

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Zn and Sn and the solution was stabilized by addition of an ethylamine. The EHD jet printing system (EHD-jet100, Teraleader) was used with an orifice size of 500 μm. Uniform spray droplet ejection was tested by adjusting an applying, pulse rate, spray distance to substrate with the substrate temperature. After EHD jet spray of ZTO solution on the 300 nm thick thermally grown silicon oxide gate insulator on the heavily doped silicon wafer, the films were then thermally annealed at the temperature of 600°C for one hour. Aluminum (Al) as source and drain electrode (S-D) was also deposited by thermal means with the TFT channel of 1500-μm width and 100-μm length. All current voltage (*I-V*) characterizations of the ZTO TFT were carried out with a semiconductor parameter analyzer (Keithley 4200) in the dark at room temperature.

3. RESULTS AND DISCUSSION

EHD spray-deposition technique has a unique system with various parameters to be carefully controlled because of delicate system as shown in Fig. 1. The solution was adjusted its concentration to spray in proper format on the substrate. Applying a voltage to the solution was a critical factor to control the output type of solution through the nozzle. Higher voltage causes the narrow shaped spray but the spray was bent to different shape. Low voltage could not produce a proper spray, so that EHD nozzle spray did not make continuous film. After spraying, the solvent should be evaporated to sustain a suitable film formation at certain temperature and atmosphere. The next factor was the pressure of syringe, this should be considered together with the applied voltage to produce suitable spray pattern. The next factor was the distance between nozzle and substrate. The last factor was EHD spraying time. However, EHD spray-deposited film was also controlled by the complex factors in the system. This is a completely different mechanism to spray or spray pyrolysis, in which major factor is the applying pressure to a solution to spray. After careful test of these factors, we established optimized process parameters, such as electrical voltage to apply nozzle of 3 KV, solution pursing of 0.032 μl per sec, the distance between nozzle and substrate of 45 mm for 30 sec with a 0.3 M of ZTO solution at RT and 50°C. The EHD spray-deposited pattern was monitored by microscope to check the spray time and deposition figures.

Optical microscopic images of sprayed solution ZTO were investigated as shown in Fig. 2. The two different substrate temperature conditions were 25°C at 3 KV for 30 sec (a) and 75°C at 3 KV for 30 sec (b), respectively. As you can see the droplet sizes of solution ZTO were varied with applied voltage, large droplets with low voltage and small droplets with high voltage. We obtained the droplet sizes from 30 - 40 μm with 3 KV at 75°C and from 70 - 80 μm with 3 KV at 25°C, respectively.

The XRD spectra of ZTO after thermal annealing at 600°C for one hour was the same as our previous reports (not shown here).[7] XRD spectra exhibited three amorphous-like broad peaks, located at around 22 degrees, 33 degrees, 50 degrees. These peaks represented the major diffraction peaks

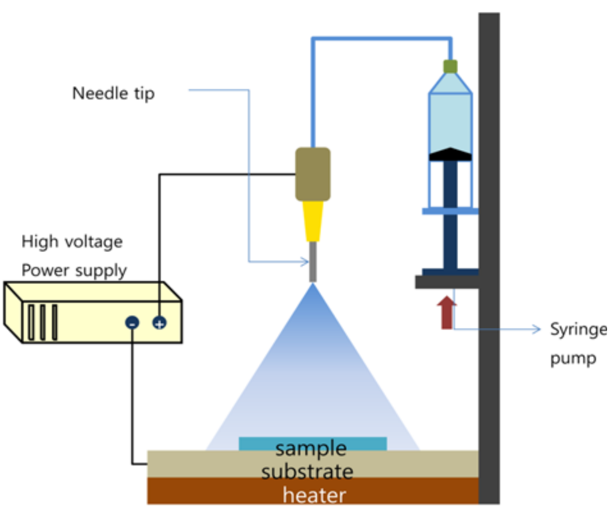

Fig. 1. Schematic of electrohydrodynamic (EHD) spray system.

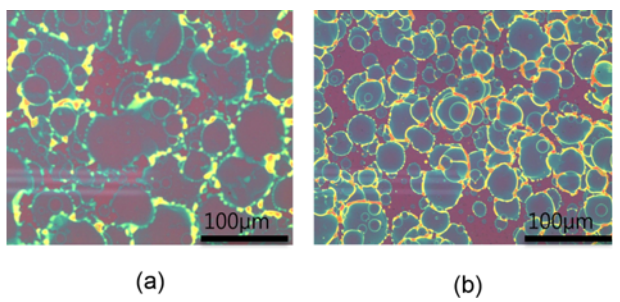

Fig. 2. Optical microscopic images of different sprayed condition; (a) 25°C of substrate temperature at 3 KV, (b) 75°C of substrate temperature at 3 KV for 30 sec.

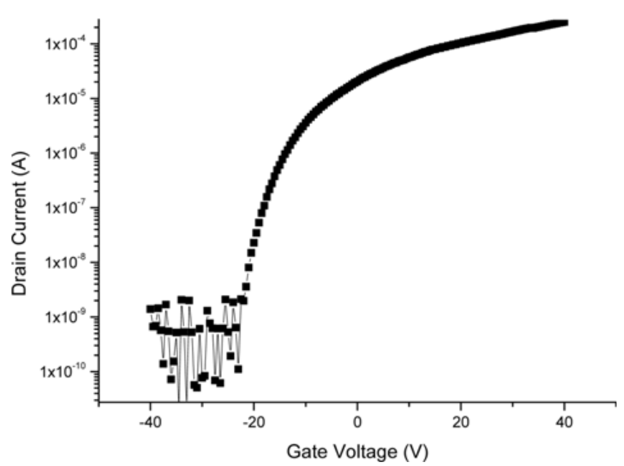

Fig. 3. Transfer characteristic of EHD-sprayed ZTO TFT.

of crystalline $ZnSnO_3$, Zn_2SnO_4, and SnO_2. Another peaks at around 27 degrees arose with the temperature of above 600°C, indicating (110) crystallinity. This is the thermodynamically the most stable and predominant crystal surface.

Figure 3 showed the transfer characteristics of Id versus Vg at $V_d = 40$ V for the EHD spray-deposited ZTO TFTs at 3 KV with substrate temperature of 50°C. The electrical properties, such as saturation mobility, threshold voltage, and subthreshold slope, were derived from a linear fitting to the plot of the square roots of I_d versus Vg using the general saturation equation. The electrical properties of ZTO TFT after annealing were a mobility of 2.0 $cm^2\ Vs^{-1}$, a threshold voltage of −10 V, a subthreshold slopes of 1.74 V dec^{-1}, and an on-to-off ratio of 10^5. This result is really comparable of other solution processed ZTO TFTs.

Figure 4 showed the drain current versus drain voltage (I_d-V_d) output characteristics of the EHD spray-deposited ZTO TFT at various gate voltages. From the output characterization in Fig. 3, no crowding is observed, indicating a good contact resistance for the source-to-drain conduction.

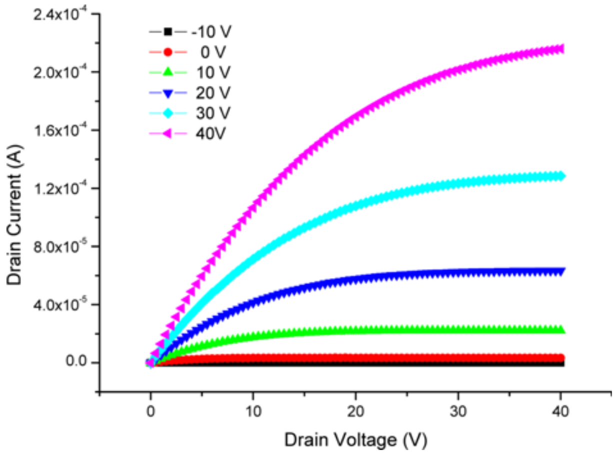

Fig. 4. Output property of EHD sprayed ZTO TFT with different gate voltages.

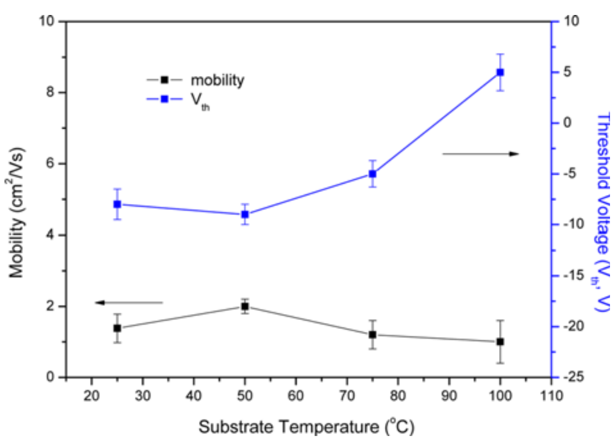

Fig. 5. Effect of substrate temperatures on mobility and threshold voltage of ZTO TFT.

Because of mutidroplets during spray, the contact was carefully controlled. The output curves measured at V_d from 0 to 40 V, exhibit clear pinch-off and solid saturation, indicating that the device follows the standard field-effect transistor theory.

As shown in Fig. 5, the effect of substrate temperatures on electrical properties was investigated. As the substrate temperature increased, mobility also slightly increased at 50°C, after then mobility decreased with temperatures with the variation of 1 cm^2/Vs to 2 cm^2/Vs. The threshold voltage of the device showed similar behavior; the threshold voltage decreased at 50°C, and then the voltage gradually increased with the temperatures with the variation of −10 V to 5 V. As the substrate temperature increased, the threshold voltage shifted to right direction. The operation of EHD sprayed ZTO TFT was changed from depletion mode to enhancement mode with the substrate temperature. This might be due to the less charge trapping in the sprayed oxide semiconductor and the interface between semiconductor and oxide dielectric. The optimal substrate temperature for the electrical properties was 50°C due to the suitable solvent evaporation and film formation for the device.

EHD is a unique technique. We successfully prepared EHD sprayed solution ZTO TFT with electrical properties. And we found a possibility as a solution processable printing method for the further research and applications.

4. CONCLUSIONS

We successfully prepared EHD sprayed solution ZTO TFT for the first time. The optimized EHD spray parameter was established. The electrical properties showed a mobility of 2.0 cm^2/Vs, a current ratio I_{on}/I_{off} of 10^5, a threshold voltage of −10 V, a subthreshold slope of 1.74 V/dec. This electrical property was relatively good comparing to other solution-processed ZTO TFT. More in-depth research should be performed in this specific area for further development and electronic applications.

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