

# Fabrication of Solution Processed Thin Film Transistor Using Zinc Oxide Nanoparticles

**Sul Lee, Sunho Jeong, Dongjo Kim, Bong-Kyun Park, and Jooho Moon\***

**Department of Materials Science and Engineering,**

**Yonsei University, Seoul 120-749, Korea**

**Phone: 82-2-2123-2855, E-mail: jmoon@yonsei.ac.kr**

## Abstract

*Zinc oxide nanocrystals are attractive candidates for a solution-processable semiconductor for high performance thin film field effect transistors. We have studied ZnO thin film transistor fabricated by solution process and have improved  $V_{th}$  by controlling the ZnO ink additives. Synthesized ZnO nanoparticles of 30nm were dispersed in solvent to make the ZnO ink. ZnO ink was spin coated on silicon wafer and after heat treatment electrodes were patterned.*

## 1. Introduction

There is currently significant interest in realizing high performance thin-film transistors (TFTs) based on solution processable semiconducting materials for applications requiring low-cost, low-temperature manufacturing for large area display devices [1-3]. For the past few years organic semiconductor such as pentacene, Poly(3-hexylthiophene) (P3HT) and  $\alpha,\omega$ -dihexyl-quaterthiophene (DH4T) have been expected to be alternatives to polycrystalline silicon in large area display [4-6]. However, despite of their low-cost and low-temperature manufacturing, their abilities are limited. Although pentacene shows the largest channel mobility among the organic TFTs, it is reported that the theoretical limit of channel mobility is  $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  and most of the organic materials are sensitive of humidity [7-9]. For this reason, inorganic material, especially, ZnO that is an n-type, wide band gap semiconductor with various applications such as varistors and light emitting diode, has been focused [10]. Recently, ZnO is utilized as active channel layers in thin film transistor because it is stable in air and compatible for solution process. The recent demonstration of an engineered inorganic TFT with a mobility of  $80 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  suggests that there is much room for further improvement [11].

In this work, we here developed a semi-conductive ink which contains zinc oxide nanoparticles. The ink was used to form active layer by spin coating. Solution processability offers a simple and low-cost processing alternative to vacuum deposition. Because of defects and grain boundary, however, spin coated thin film ZnO usually shows poor mobility than crystallized ZnO, so the films need to be annealed for particle neck growth. This study was focused on improving the particle connectivity. Baoquan Sun et al. used post-deposition hydrothermal growth to enhance grain size and connectivity [12]. In our study, zinc acetate was added to ink for growing particle neck during annealing.

The synthesized particles were characterized by SEM and XRD. Saturation mobility and threshold voltage for solution-processed TFT were characterized by I-V measurement.

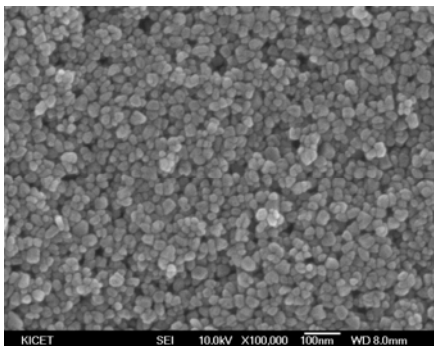
## 2. Results

Spin coated ZnO film was used as channel layer, together with Cr/Au source-drain electrode and 200 nm thermal silicon oxide wafer as dielectric.

### 2.1. ZnO Particles Synthesis and Ink Preparation

Starting with zinc acetate, zinc oxide nanoparticles which have a size of about 30 nm were synthesized by polyol process as seen in Figure 1 [13]. Diffraction peaks of the particles were well matched with hexagonal wurtzite-structure ZnO peaks, indicating phase-pure crystalline nanosized ZnO. For the preparation of the spin-castable ink, the ZnO particles were dispersed in a mixed solvent of ethylene glycol (EG) and 2-methoxyethanol and mixed by ball-milling. The solid loading of zinc oxide powder was 10 wt%. Dispersion stability of prepared ZnO inks was excellent and the inks exhibit

Newtonian rheological behavior. A viscosity of the ZnO ink was 6-7 mP · s.



**Figure 1. SEM image of synthesized ZnO nano particles**

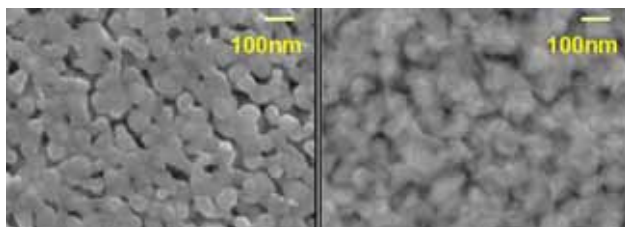
Table 1 show two types of ink we used. Ink 1 contained only ZnO particles and 0.4M of zinc salt is added to ink 2 in order to enhance the connectivity between ZnO particles to the ZnO ink prior to spin coating.

**Table 1. Composition of two types of ink prepared as semiconducting material**

	ZnO	Solvent	Additive
Ink 1	10wt%	EG/2-methoxy-Ethanol	None
Ink 2	10wt%	EG/2-methoxy-ethanol	0.4M Zinc acetate

**2.2. Film Formation**

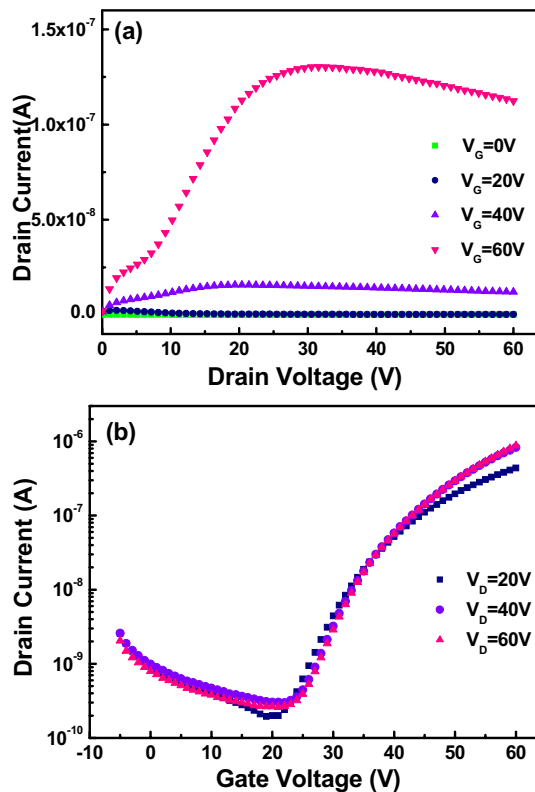
As shown in table 1, two types of inks were prepared for forming channel layer. The inks were spin coated 2000 rpm, 30 sec on SiO<sub>2</sub>/n-type Si. After spin coating the samples were heated to 600°C for 5 hours. Synthesized 30nm ZnO particle formed neck when heated over 500°C. As expected, the film with type 2 ink has shown better connectivity and more smooth surface (Figure 2).



**Figure 1. ZnO particles (left) and zinc acetate added ZnO (right) after annealing**

**2.3. Device Characteristics**

In order to improve the reaction of zinc acetate to zinc oxide and to reduce defects in ZnO such as oxygen vacancy, annealing process was performed in oxygen atmosphere. After the annealing, the electrodes were patterned by a thermal evaporator.



**Figure 2. Output and transfer behavior of ZnO film annealed in oxygen**

Figure 3(a) and (b) show the drain current-drain voltage ( $I_D$ - $V_D$ ) characteristics and the drain current-gate voltage ( $I_D$ - $V_G$ ) characteristic of solution processed ZnO-based TFT fabricated using the ink 1. As shown in Figure 3, the saturation mobility of ZnO transistor was  $2 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and threshold voltage was 31 V by oxygen atmosphere and it was notable that the mobility increased about 2 orders of the magnitude compared to that of annealed in air which was  $2 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ . We found that heat-treatment in oxygen atmosphere makes the oxygen defect decreased, so that mobility could be increased. It is known that empty oxygen sites could trap charge carrier. If the oxygen vacancy is reduced, the carrier can move more freely [14]. For this reason, all

transistors were annealed in oxygen atmosphere. When we used ink 1 for channel, 30V of gate voltage was needed to operate the device. Drain current behavior when  $V_G = 0V$  was relatively identical with that when  $V_G = 20V$ . (Figure 3 (a)) That corresponds to the gate voltage – drain current data in figure 3(b).

When ink 2 was used for semiconductor material and annealed at  $600^\circ C$  in  $O_2$ , the mobility was  $3 \times 10^{-3} cm^2 V^{-1} s^{-1}$  and the threshold voltage was decreased to  $-1V$  (Figure 4). Zinc acetate has been already used to make ZnO film by sol-gel process with 2-methoxyethanol [15-16]. It is known that zinc acetate transform to ZnO with heating. The temperature for the transformation is little different according to the papers, however,  $600^\circ C$  seems to be sufficient. When XRD diffraction patterns were observed, the diffraction peaks were well matched with ZnO peaks, so it could be concluded that added zinc acetate transforms to ZnO during the annealing.

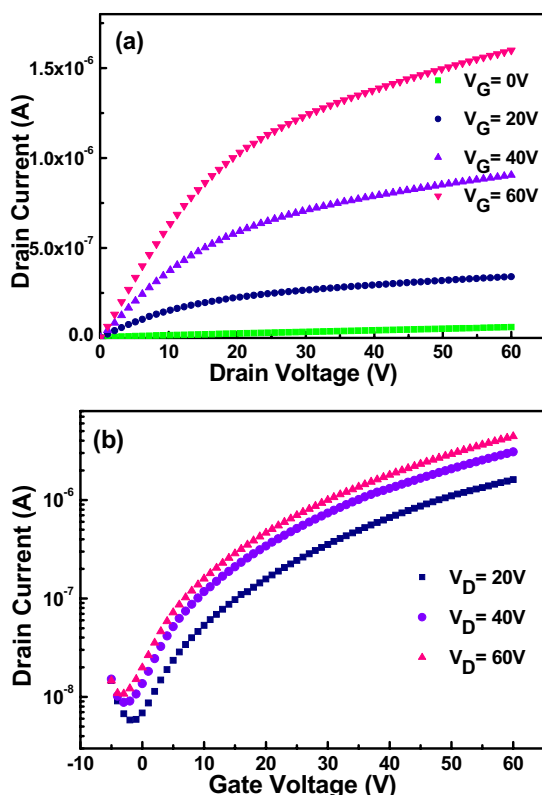


Figure 3. Output and transfer behavior with zinc acetate added ZnO film annealed in oxygen

As compared with device with ink 1, the device from ink 2 has more little threshold voltage. Decrease in the threshold voltage comes from the neck growth with an aid of the zinc acetate. Usually, there are some pores between particles to particle. In comparison, during the  $O_2$  heat treatment, zinc acetate transforms to ZnO and it enhances the connectivity among the particles. It is known that grain boundary acts as an energy barrier, so that gate bias lowers the barrier height [17]. The smaller grain size led to more energy barrier, thus it hinders the charge carrier in the movement. When zinc acetate becomes ZnO and fills the space, especially the neck of particles, it helps the accumulation of charge as well as the formation of shorter transportation pathway. The mobility of two kinds of transistors is similar to each other. Addition of zinc acetate to the ink improved the threshold voltage.

### 3. Conclusion

Solution processed ZnO TFT has been studied for large area and low cost electronic device. In this paper, ZnO film was fabricated from the crystalline ZnO nanoparticles. The channel mobility was improved by heat treatment in oxygen atmosphere. Zinc acetate added into ink improved the operating voltage but unchanged the carrier concentration of ZnO film. Despite of that, this particle-based fabricating method would be applicable to ink-jet printing and the addition of zinc acetate would be a hint to enhance the performance of solution processed ZnO thin film transistors.

### 4. Acknowledgements

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### 5. References

- [1] M. Mushrush, A. Facchetti, M. Lefenfeld, H.E. Katz, T.J. Marks, J. Am. Chem. Soc. **125**, 9414 (2003).
- [2] A. Afzali, C.D. Dimitrakopoulos, T.L. Breen, J. Am. Chem. Soc. **124**, 8812 (2002).
- [3] H. Sirringhaus, T. Kawase, R.H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, E.P. Woo, Science **290**, 2123 (2000).
- [4] F. Garnier, R. Hajlaoui, A. E. Kassmi, G.

- Horowitz, L. Laigre, W. Porzio, M. Armanini, F. Provasoli, *Chem. Mater.* **10**, 3334 (1998).
- [5] J. Chang, B. Sun, D. W. Breiby, M. M. Nielsen, T. I. Sölling, M. Giles, I. McCulloch, H. Sirringhaus, *Chem. Mater.*, **16**, 4772 (2004)
- [6] J. Lee, S. Kim, G. Kim, S. Lim, H. Lee, J. Jang, T. Zyung, *Synthetic Metals* **139** 445 (2003)
- [7] C.D. Dimitrakopoulos, P.R.L. Malenfant, *Adv. Mater.* **14** , 99 (2002).
- [8] H.E. Katz, A.J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y.Y. Lin, A. Dodabalapur, *Nature* **404**, 478 (2000).
- [9] E.Fortunato, A. Pimentel, L. Pereira, A. Gonçalves, G. Lavareda, H. Aguas, I. Ferreira, C.N. Carvalho, R. Martins, *J. Non-cryst. Sol.* **806**, 338 (2004).
- [10] J. H. Lee, *Electrochemical and Solid-State Letters*, **9**, G117 (2006)
- [11] B. J. Norris, *J. Phys. D: Appl. Phys.* **36**, L105 (2003)
- [12] B. Sun, and H. Sirringhaus, *Nano Lett.* **5**, 2408 (2005)
- [13] L. Poul, *Solid State Science.* **3**, 31 (2001)
- [14] V. Ischenko, S. Polarz, D. Grote, V. Stavarache, K. Fink, M. Driess, *Adv. Funct. Mater.* **15**, 1945 (2005)
- [15] H. Jozuka, and T. Yoko, *J. Am. Ceram. Soc.* **81**, 1622 (1998).
- [16] R. B. H. Tahar, *J. Euro. Ceram. Soc.* **25**, 3301 (2005).
- [17] F. M. Hossain, *J. Appl. Phys.* **94**, 7768 (2003).