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Solution-processed ZnO nanoparticle-based semiconductor oxide thin-film transistors

Sul Lee [a], Youngmin Jeong [a], Sunho Jeong [a], Jisu Lee [b], Minhyon Jeon [b], Jooho Moon [a,*]

[a] *Department of Materials Science and Engineering, Yonsei University, 134 Shinchon-dong Seodaemun-gu, Seoul 120-749, South Korea*

[b] *Department of Nano Systems Engineering, Inje University, Gimhae, Gyongnam, 621-749, South Korea*

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ABSTRACT

We have prepared solution-processed oxide semiconductor thin-film transistors using ZnO nanoparticles with various particle shapes. Uniform, dense, thin films were produced by spin-coating ZnO nanoparticle dispersions containing either nanorods or nanospheres. The influence of annealing atmosphere on both nanoparticle-based TFT devices was investigated. XPS analysis revealed that the ZnO particles of the nanorod and nanosphere dispersions have distinct stoichiometries (i.e., molar ratios of Zn:O). The starting particles in turn predetermine the carrier concentration within the annealed ZnO films, which in turn determines whether the device is a semiconductor or metallic conductor, depending upon the annealing atmosphere. Grain structures of the channel layer also play an important role in determining the device performance of the nanoparticle derived ZnO TFTs.

1. Introduction

Thin-film transistors (TFT) have been generally fabricated by vacuum deposition methods such as ion beam sputtering and pulsed laser deposition. Recent years have seen a growing interest, however, in producing printed TFTs using solution-processable materials for applications in which low-cost, low-temperature manufacturing is required [1–3]. To realize printed TFTs, it is essential to develop semiconductor ink materials from which the semiconducting channel layers are produced by a simple

* Corresponding author. Tel.: +82 2 2123 2855; fax: +82 2 365 5882.
E-mail address: jmoon@yonsei.ac.kr (J. Moon).

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coating or printing method. It is difficult to fabricate poly-Si-based high-performance TFT at lower temperatures by solution processes such as spin coating and ink-jet printing. Amorphous silicon has been introduced as a low-cost channel material; however, its TFT mobility values are less than 0.1 $cm^2\ V^{-1}\ s^{-1}$ [4].

Solution-processable organic semiconductors such as poly[5.5′-bis(3-dodecyl-2-thienyl)-2.2′-bithio-phene] (PQT-12), poly(3-hexylthiophene) (P3HT), α, ω-dihexyl-quaterthiophene (DH4T) have been also investigated, but they suffer low mobility (below 0.1 $cm^2\ V^{-1}\ s^{-1}$) and poor stability against humidity [5–7]. For this reason, solution-processable inorganic materials that are stable in air and suitable for solution processes have drawn recent research interest. Zinc oxide (ZnO) is a direct wide-band gap semiconductor ($E_g = 3.37$ eV), making it an excellent candidate for UV light-emitting diodes (LEDs), lasers, and transparent transistors [8,9]. The conduction band of ZnO is primarily composed of large, metal 4s orbitals spread out spatially with isotropic shapes, such that direct overlap among neighboring metal orbitals is possible. These unique properties led to recent interest in ZnO as a channel material alternative to conventional Si-based materials and organic semiconductors. As a precursor for producing ZnO films, various materials such as dissolved metal halides, acetates, and nanoparticles have been utilized. In particular, ZnO nanoparticles are attractive candidates for manufacturing printed TFTs at low cost and low temperature on large-area, flexible substrates [10–14].

We have created solution-processed semiconductor oxide TFTs by spin coating from ZnO nanoparticle dispersion. In our previous study, the particle-based ZnO semiconductor films were fabricated with ZnO synthesized by the polyol method [15]. In addition to spherical ZnO, nanorods are used to fabricate spin-coated ZnO nanocrystal semiconductor films. ZnO particle morphology and annealing atmosphere both play important roles in controlling TFT device performance.

2. Experimental

ZnO nanoparticles with two different morphologies were prepared by a polyol method that involves hydrolysis of zinc acetate salt in an organic solvent [16]. Detailed synthesis methods were described in our previous work [17]. For synthesis of the spherical ZnO particles, zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Aldrich) was dissolved at 25 °C in diethylene glycol (DEG, 99.9% Aldrich). Polyvinylpyrrolidone (PVP, $M_w = 10{,}000$ g/mol, Aldrich) was also dissolved to prevent the synthesized particles from agglomerating. The precursor solution was heated under vigorous stirring, and deionized water was injected into a hot Zn acetate-dissolved DEG solution at 180 °C. The reaction maintained for 30 min and was followed by cooling to room temperature. The particles were separated from the liquid by centrifugation and then repeatedly washed with methanol. For rod-like particles, both zinc acetate dihydrate and deionized water were added into the PVP dissolved DEG at 25 °C. This precursor solution was heated to 180 °C and stirred vigorously. The reaction was continued for 30 min after the temperature reached 180 °C. The particle recovery procedures were identical to those previously described. Fig. 1(a) and (b) show SEM images of the synthesized ZnO particles of rod- and sphere-like shapes. The average major axis and minor axis lengths for the rod-shaped particles are 114 ± 54 nm and 31 ± 10 nm, giving an aspect ratio of 3.6, while the average diameter of the spherical particles is 24 ± 4 nm. The particles obtained at 180 °C are crystalline ZnO with wurtzite crystal structures as confirmed by XRD analysis (Rigaku, D/max-Rint 2000).

Spin-castable inks (i.e., ZnO nanoparticle suspensions) were prepared by dispersing the synthesized particles in a mixed solvent of ethylene glycol and 2-methoxyethanol at the solid loading of 10 wt%. The ZnO suspension should be dilute and well-dispersed to achieve a low viscosity. The rheological measurement (DV–III, Brookfield) revealed that the ZnO inks were well-dispersed with a viscosity of 6.5–7.0 mPa s at 90 s^{-1}, showing nearly Newtonian flow behavior. TFT devices of a bottom-gate, bottom-contact structural configuration were built on a heavily doped silicon substrate with 200 nm-thick SiO_2 dielectric using a solution-processed semiconductor. The substrates were cleaned by piranha solution (sulfur acid:hydroperoxide = 4:1) and rinsed with deionized water twice prior to use. The ZnO inks containing either spherical or rod-like particles were spin-coated on the SiO_2 surface. After spin coating at 2500 rpm for 30 s, the films were annealed at 200–600 °C for 5 h or 700 °C for 1 h in either air or an oxygen atmosphere. Au (50 nm) source and drain electrodes