

# Effects of zirconium doping on the characteristics of tin oxide thin film transistors



Dong-Suk Han<sup>a</sup>, Jae-Hyung Park<sup>a</sup>, Yu-Jin Kang<sup>a</sup>, Jong-Wan Park<sup>b,\*</sup>

<sup>a</sup> Department of Nanoscale Semiconductor Engineering, Hanyang University, 17 Haengdang-dong, Seoungdong-ku, Seoul 133-791, Republic of Korea

<sup>b</sup> Department of Materials Science and Engineering, Hanyang University, 17 Haengdang-dong, Seoungdong-ku, Seoul 133-791, Republic of Korea

## ARTICLE INFO

### Article history:

Received 23 January 2013

Received in revised form 28 May 2013

Accepted 2 July 2013

Available online 27 July 2013

## ABSTRACT

Thin-film transistors (TFTs) with zirconium-doped tin oxide (ZSO) channels were fabricated by co-sputtering Sn and Zr metal targets. The effect of Zr on the performance of SnO<sub>x</sub>-based TFTs was studied. TFTs with an intrinsic SnO<sub>x</sub> channel did not show promising performance. However, ZSO TFTs exhibited improved electrical properties, with increased  $I_{ON}/I_{OFF}$  and decreased subthreshold swing. The influence of zirconium doping on bias stability in tin oxide TFTs was also investigated. ZSO TFTs exhibited turn-on voltage ( $V_{ON}$ ) shifts of +9 V for positive stress bias, compared with +18 V for intrinsic SnO<sub>x</sub> TFTs. The improvements in device performance and stability were attributed to reduced carrier concentration induced by carrier trapping at Zr impurity sites.

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## 1. Introduction

Transparent ZnO-based thin-film transistors (TFTs) have been studied intensively as an alternative active-matrix backplane for active-matrix liquid crystal displays (AMLCD), active-matrix organic light emitting displays (AMOLED), and flexible displays. TFTs are potential candidates due to their high mobility ( $>10 \text{ cm}^2/\text{Vs}$ ) and relatively good stability compared with amorphous Si TFTs [1–4]. InGaZnO semiconductors have received considerable attention since a report by Nomura et al. demonstrated the fabrication of flat panel displays that utilize amorphous InGaZnO TFTs as active matrix backplanes [5,6]. Although oxide TFTs such as InGaZnO are promising alternatives to conventional backplanes, several obstacles that have delayed their incorporation into commercial products have not been investigated in detail. The conduction band minimum (CBM) of InGaZnO TFTs is mainly formed by In ions, which are responsible for high channel mobilities. However, In is a rare material that may become seriously depleted if overexploited. Further, accurate and repeatable control of complex materials is difficult in mass production contexts. Therefore, less complex oxide compositions that can replace In must be identified. The use of tin-based oxide semiconductors as a channel layer for TFTs has been investigated. Because tin ions (e.g.,  $\text{Sn}^{4+} \cdot 4d^{10}5s^0$ ) have orbitals similar to those of indium ions ( $\text{In}^{3+} \cdot 4d^{10}5s^0$ ), high mobility can be expected [7]. Tin oxide has been used as component in transparent conductive oxides such as indium tin oxide (ITO). However, its application in the active channels of TFTs has been limited due to the difficulty of controlling the net electron

density ( $N_d$ ) ( $<10^{17} \text{ cm}^{-3}$ ) [8,9]. High net carrier densities have limited the applications of TFTs with SnO<sub>x</sub> semiconductors. Thus, the stability of SnO<sub>x</sub>-based TFT devices remains a crucial issue.

In this article, we report the fabrication of TFTs with SnO<sub>x</sub> films as channel layers via Zr doping. The addition of Zr to SnO<sub>x</sub> thin films affects the carrier concentrations and electron mobilities of TFT devices. Furthermore, zirconium–tin oxide (ZSO) TFTs show improved bias stability. The origin of improvements in ZSO TFTs and the electrical role of Zr in SnO<sub>x</sub> semiconductors suggest that the electrical role of Zr in SnO<sub>x</sub> semiconductors may be similar to that of Ga in InGaZnO semiconductors. This will be discussed later in detail [10].

## 2. Experimental

Fig. 1 shows a cross-sectional schematic of a bottom-gate-type ZSO TFT with a staggered structure prepared on a heavily-doped n-type silicon substrate with a buffered gate insulator (plasma-enhanced chemical vapor deposited SiO<sub>2</sub> layer of 10 nm/low pressure chemical vapor deposition SiN<sub>x</sub> layer of 100 nm). Thin films of ZSO 40 nm thick were deposited using a DC magnetron sputtering system. The Zr concentrations in SnO<sub>x</sub> were controlled by plasma discharge power density. The input plasma discharge power density of the Sn target was fixed at  $0.5 \text{ W/cm}^2$ , while that of the Zr target varied from 0.06 to  $0.127 \text{ W/cm}^2$ . Sputtering was performed at room temperature in an argon atmosphere with an oxygen partial pressure of 50%. The 4-inch-diameter target was placed 4 cm from the substrate. A base pressure of  $2.7 \times 10^{-4} \text{ Pa}$  and a working pressure (Ar + O<sub>2</sub>) of  $6.6 \times 10^{-1} \text{ Pa}$  were used. The channel and source/drain contacts were patterned using shadow masks. Channel length and width/length ratios were 100 μm and 10:1,

\* Corresponding author. Tel.: +82 222200386; fax: +82 222982850.

E-mail address: [jwpark@hanyang.ac.kr](mailto:jwpark@hanyang.ac.kr) (J.-W. Park).

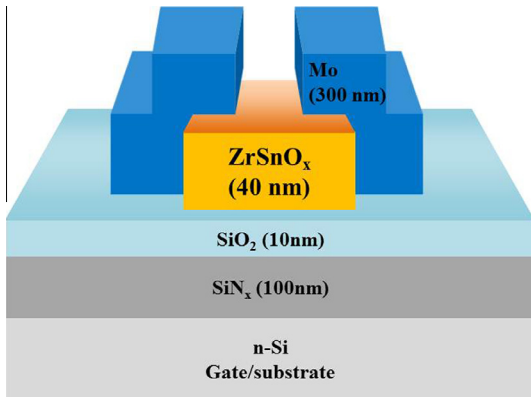


Fig. 1. Cross-sectional schematic of bottom-gate-type ZSO-based TFT with staggered structure.

respectively. After Mo electrode deposition, the devices were subjected to thermal annealing at 150–200 °C for 60 min in ambient air. The atomic contents of Zr in ZSO films was analyzed by ICPMS and found to be 1.57 and 3.24 at.%. Chemical properties of the films were analyzed using X-ray photoelectron spectroscopy (XPS, ESCA lab 220, VG Microtech). This system uses Mg K $\alpha$  radiation ( $h\nu = 1253.6$  eV) excitation source. The X-ray beam energy and filament current were 12 kV and 10 mA, respectively. To calibrate the energy scale after XPS analysis, the assumed reference energy was C 1 s (285.0 eV). XPSPEAK41 software was used to fit the peaks. Peak background was deleted while the peak position, FWHM, area, and Lorentzian-Gaussian parameters were constrained to de-convolute the peak. Film structures were examined by X-ray diffraction (XRD, D-2500, Rigaku) analyses using Cu K $\alpha$  radiation. Standard  $\theta$ -2 $\theta$  XRD measurements were performed at 40 kV and 30 mA. All electrical characterizations were performed with a semiconductor parameter analyzer (Agilent HP 4145B) at room temperature in the dark without a passivation layer.

### 3. Results and discussion

Fig. 2 and Table 1 shows representative transfer curves and device parameters for intrinsic SnO $_x$  TFTs and ZSO TFTs. The apparent field-effect mobility, which is defined by  $\mu_{FE} = Lg_m/WC_iV_{DS}$ , was extracted using transconductance measured at a low drain voltage ( $V_{DS} \leq 1$  V). In this equation,  $C_i$  and  $g_m$  are the capacitance per unit area of gate insulator and transconductance, respectively. The

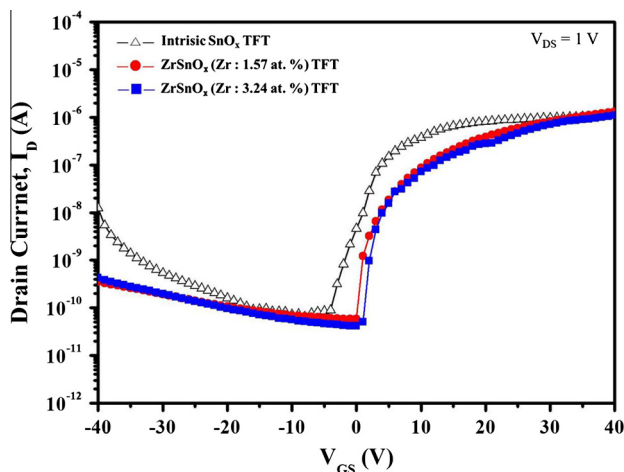


Fig. 2. Transfer characteristics of ZSO TFTs as a function of Zr content. Devices had a width of 1,000  $\mu$ m, length of 100  $\mu$ m, and  $V_{DS} = 1$  V.

field-effect mobilities ( $\mu_{FE}$ ) decreased to  $\sim 0.95$  cm $^2$ /Vs at Zr levels of 3.24 at.%. Field-effect mobility is greatly affected by the density of the trailing state near the conduction band (shallow trap). Since subthreshold gate swing (SS) is determined by the deep-level trap density, the SS was decreased from 0.91 to 0.78 V/decade as Zr content increased. The SS values were extracted from the linear portion of the log  $I_{DS}$  versus  $V_{GS}$  plot by the following equation:

$$SS = \frac{dV_{GS}}{d(\log I_{DS})}. \quad (1)$$

Furthermore, SS value is an indicator of the total trap density ( $N_t$ ). This includes the bulk trap density ( $N_{bulk}$ ) of the amorphous ZSO semiconductor and the interface trap density ( $D_{it}$ ) at or near the interface between  $\alpha$ -ZSO and SiO $_2$ /SiN $_x$ . Total trap density can be calculated using the following equation [11]:

$$N_t = \left[ \frac{SS \log(e)}{kT/q} - 1 \right] \frac{C_i}{q}. \quad (2)$$

Compared with intrinsic tin oxide TFTs (0.91 V/decade) improved gate swing of zirconium-doped tin oxide TFTs (0.76 V/decade) can be attributed to the reduction of  $N_t$ .

Previous studies have suggested that Zr ions act as oxygen binders in ZnSnO TFT, resulting in reduced carrier concentration due to reduced  $V_O$  (oxygen vacancy) defect density [12]. Similarly, in this study, the addition of low levels of Zr suppressed carrier concentration. The carrier concentration of SnO $_x$  films has been related to crystalline structure, oxidation state, and oxygen deficiency. The decrease in carrier concentration and mobility in this study may be related to changes in the oxidation state of Sn. This is consistent with the following XPS results and observations of low Al doping in SnO $_x$  films [13]. The decrease in the SS of ZSO TFTs attributed to lower trap densities in deep-level states in the channel layer, including interface trap and bulk trap densities.

XRD and XPS analysis were used to investigate possible explanations for changes in the device characteristics of ZSO TFTs. Fig. 3 shows XRD patterns of 40-nm-thick ZSO (Zr: 3.24 at.%) films with increased annealing temperature, from 25 °C (pristine, room temperature) to 600 °C. The absence of any XRD peak for pristine and annealed samples with the 200 °C ZSO films indicates an amorphous structure. However, the ZSO films annealed at 400 °C and 600 °C shows a crystalline phase, with diffraction peaks assigned to the (110), (101), (200), and (211) reflections of SnO $_2$  crystal. Regardless of Zr incorporation, all ZSO films annealed below 200 °C had an amorphous structure, so grain boundary trapping effects were excluded.

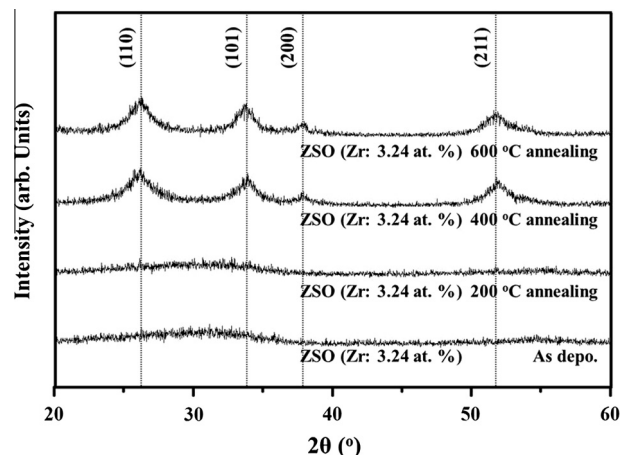


Fig. 3. XRD patterns of ZSO films annealed at 200, 400, and 600 °C compared with as-deposited film.

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