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Sections

Governance and
Committees

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Table of Contents

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[ISSUE INDEX](#)

[PAGE/SECTION INDEX](#)

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[NEXT →](#)

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[Search This Issue](#)

Volume 14, Issue 12 , p. A171-S11

- [Batteries and Energy Storage](#)
- [Fuel Cells and Energy Conversion](#)
- [Electrochemical/Chemical Deposition and Etching](#)
- [Electrochemical Synthesis and Engineering](#)
- [Dielectric Science and Materials](#)
- [Semiconductor Devices, Materials, and Processing](#)
- [Sensors and Displays: Principles, Materials, and Processing](#)
- [Nanostructured Materials, Carbon Nanotubes, and Fullerenes](#)
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BATTERIES AND ENERGY STORAGE

- Electrochemical Properties of an All-Organic Redox Flow Battery Using 2,2,6,6-Tetramethyl-1-Piperidinyloxy and N-Methylphthalimide**

[Zhen Li](#), [Sha Li](#), [Suqin Liu](#), [Kelong Huang](#), [Dong Fang](#), [Fengchao Wang](#), and [Sui Peng](#)

pp. A171-A173

[Abstract](#) Full Text: [[HTML](#) [Sectioned HTML](#) [PDF](#)] [Order](#)



Effect of Indium Contents on the Solution-Processed SiInZnO Thin Film Transistors Annealed at Low Temperature

Ki-Ho Park,^{a,b} Eugene Chong,^{a,c} Byeong-Kwon Ju,^b and Sang Yeol Lee^{d,z}

^aElectronic Materials Center, Korea Institute of Science and Technology, Seoul 136-791, Korea

^bDisplay and Nanosystem Laboratory, College of Engineering, Korea University, Seoul, Korea

^cNanoelectronics, University of Science and Technology, 113 Gwahangno, Yuseong, Daejeon 305-333, Korea

^dDepartment of Semiconductor Engineering, Cheongju University, Cheongju, Chungbuk, 360-764, Korea

The effect of the indium contents (from 1 to 5 molar ratios of In) on the threshold voltage (V_{th}) and field effect mobilities (μ_{FE}) of solution processed silicon-indium-zinc-oxide (SIZO) thin film transistors (TFTs) have been reported. The negative shift of V_{th} was occurred from 4.37 to -0.75 V and the μ_{FE} was increased clearly by mainly exceeded In contents due to the increase of carrier concentration, which is related the increased of the number of free electrons associated with excess In incorporation in the SIZO TFTs. As increasing the In content, the excess In affects films formation of SIZO and leads to decrease of surface roughness. Subthreshold swing (S.S) was decreased due to reduced trap density at the interfaces between the active channel layer and the insulator with decreasing surface roughness of the SIZO films. This proposed that the characteristics of SIZO TFTs can be improved by controlling the In molar ratio in the SIZO based TFTs.

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The amorphous oxide semiconductors (AOSs) have attracted attention as the channel layers of thin film transistors (TFTs) because of many excellent characteristics, such as good uniformity, high carrier mobility, excellent device stability, good transparency, and low temperature process.¹⁻³ Recently, particularly transparent and flexible properties are popular owing to much technologies of application such as large area flat panel display and flexible display.⁴ Several zinc oxide (ZnO)-based multicomponent oxide materials, such as indium gallium zinc oxide (IGZO),^{1,5} zinc tin oxide (ZTO),² and indium zinc oxide (IZO)⁶ have been investigated for active channel layers in oxide semiconductors.

Most AOSs have generally been fabricated by the vacuum deposition methods, such as chemical vapor deposition, radio frequency (rf) magnetron sputtering, and pulsed laser deposition⁷⁻⁹ because vacuum-processed devices have good performance compared with solution-process. Nevertheless, AOSs are fabricated by the solution-based printing method, because solution-processed TFTs have many benefits, such as low cost, high throughput, and easily controlled composition ratio.

The solution-processed TFTs, such as IGZO¹⁰ and magnesium indium zinc oxide (MIZO),¹¹ are generally fabricated with a high temperature annealing process in order to obtain better TFT properties. However, silicon indium zinc oxide (SIZO)¹² thin films can be fabricated at lower temperature process than that of conventional IGZO and MIZO, which is 250°C. Therefore a critical issue for flexible display applications is decreased fabrication temperature.

Increase of indium content at SIZO solution-processed TFTs was necessary in order to improve the electrical properties such as carrier mobility. Because it has been known that heavy metal indium cations share electrons in 5s orbitals and act as electron pathways contributing to an increase in carrier mobility of TFTs.¹⁰ In this paper, we discuss the fabrication of low temperature solution-processed amorphous oxide TFTs and the study with effects of varying indium composition ratio in SIZO TFTs by solution process method with low annealing temperature at 250°C.

A 0.5 M precursor solution of SIZO was prepared by solution method, dissolving mixture of zinc acetate dehydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], indium nitrate hydrate [$In(NO_3)_3 \cdot xH_2O$], and silicon tetraacetate [$Si(OCOCH_3)_4$] in 2-methoxyethanol [$C_3H_8O_2$]. Then, monoethanolamine [C_2H_7NO] was used as a solution stabilizer, and stirred at 60°C for 24 h to form the SIZO sol-gel precursor. The molar ratio of Si:Zn was fixed at 0.05:1, and the molar

ratio of In:Zn was varied at 1:1, 3:1, and 5:1. The prepared SIZO solution thin films were deposited by spin-coating at 4000 rpm onto SiO_2 (200 nm)/heavily doped p-type Si wafer. The thickness of SIZO active channel layers was maintained around 35 nm. The important point in this study was post-annealing of the channel films at 250°C for 2 hrs. The width/length of active channel area was 250/50 μm . Finally, Ti/Au of 70 nm film was patterned for the source and drain electrodes by evaporation deposition and lift-off process.

For the analysis of the amorphous structure of solution-processed SIZO films, X-ray diffraction (XRD) measurement was performed. To examine the possible chemical reactions of SIZO solution precursor, thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC) were performed in an air ambience. Also, we carried out field-emission scanning electron microscopy (FE-SEM) analysis to examine the structural properties of SIZO thin film. The electrical characteristics of SIZO TFTs were measured with semiconductor parameter analyzer.

XRD data has been observed depending on In molar ratio of SIZO thin films as shown in Fig. 1a. It indicated that the SIZO films were formed as amorphous structure regardless of the In content ratio even at low temperature annealing process due to Si.¹² The ns-orbitals of metal elements such as In_2O_3 and ZnO have the potential to form conduction band bottoms, which work as electron transport paths, in amorphous semiconductors.¹³ Figure 1b shows the thermal behavior of the SIZO precursor with In molar ratio. Endothermic behavior was observed with abrupt weight loss at about 80°C. This result indicated the thermal decompositions of the added stabilizer and the used organic solvents such as 2-methoxyethanol. The large exothermic peaks observed around 233°C are interpreted as the alloying of metal hydroxides to the multi-component oxides. The weight loss which is accompanied with this exothermic peak corresponds to dehydration of the metal hydroxides.¹⁴ We expect that the SIZO thin films would be formed amorphous structure because the crystallization of SIZO precursor was not occurred in the thermal analysis.

Figure 2 shows plane view SEM image of SIZO thin films, which Si:In:Zn ratios are (a) 0.05:1:1, (b) 0.05:3:1, (c) 0.05:5:1 as varying In molar ratio. SEM image indicated that the cluster size was a little changed as increasing In contents in an amorphous structure. The Si that was incorporated into the matrix disturbed the crystal growth of IZO thin film then amorphous structure of SIZO thin films were formed, resulting in the decrease of the nano-sized particles similar to the reported other IZO-based systems.¹⁰ The surface roughness decreased with increasing In composition. This is related to the solubility

^z E-mail: sylee@cju.ac.kr

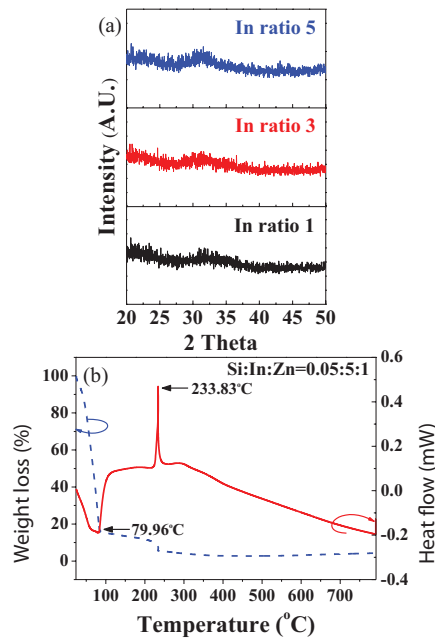


Figure 1. (a) XRD pattern of SIZO film as a function of indium molar ratio. The SIZO layer annealed at 250°C in air for 2 hrs. (b) TGA/DSC curves of the SIZO solution precursor in the indium content of 5.

limit,^{9,15,16} due to incorporation of In into the SIZO. The structure of the ZnO_m blocks is very similar to that of wurtzite ZnO .¹⁷ In contrast the InO_2^- has a cubic structure. Therefore the In^{3+} is not incorporated into the SIZO solution because of the solubility limit which can result the cubic stacking faults of InO_2^- in the SIZO films.⁹ This obstructs the form of cluster of SIZO resulting in a decrease of the surface roughness.

Figure 3 show the XPS results of the O 1s and In 3d peaks of the SIZO thin films. As shown in Fig. 3a, the O 1s binding energy in SIZO shows two main peaks. To investigate the oxygen vacancies in SIZO films, we compared the shift of two main peaks. The binding energies were shifted to higher binding energy level from 529.39 eV to 529.53 eV and from 530.68 eV to 530.76 eV at M–O bonds peaks and O–O bonds of O 1s peaks with increasing In content in the SIZO thin films, respectively.¹² It indicated that the number of free carriers was increased because oxygen vacancies were increased with increased In molar ratio. In Fig. 3b, the binding energies of In 3d_{5/2} and In 3d_{3/2} peaks associated with oxygen binding were increased with added In

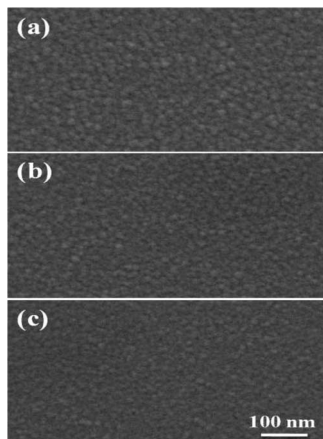


Figure 2. SEM plane view images of the solution processed SIZO films with In/Zn composition ratio of (a) 1, (b) 3, (c) 5.

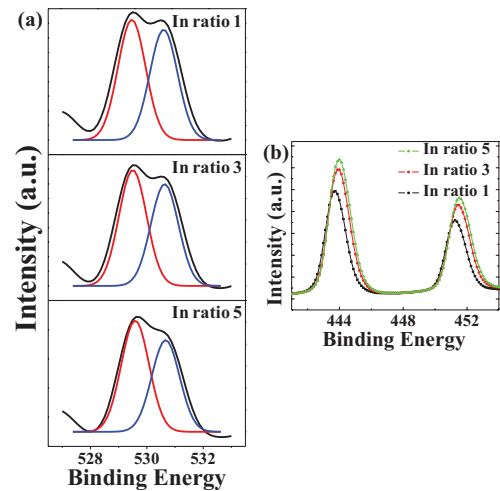


Figure 3. XPS spectra of (a) O 1s and (b) In 3d binding energy for solution-processed SIZO film annealed at 250°C.

content in the thin films. XPS spectra shows that the precursors of silicon, zinc, and indium were completely decomposed by the substitution reaction with water to form oxidized metals during annealing process.^{18,19}

Figure 4 shows the transfer curve of TFTs using solution-processed SIZO thin films as active channel layer with varied In contents. The V_{th} was shifted to negative direction from 4.37 to -0.75 V when In contents were increased. The carrier concentration (N_{cp}) was increased from 8.55×10^{16} to 2.14×10^{17} as indium molar ratio increased from 1 to 5, respectively. This is mainly due to the increase of the number of free electrons associated with the increasing indium content. The increase in In molar ratio gives rise to a larger number of oxygen vacancies and zinc interstitials, which results in more free electrons.¹⁵ The field effect mobility (μ_{FE}) increases from 5.04×10^{-5} to 4.59 with the increase of In ratio from 1 to 5. Exceeded indium atoms in the SIZO active layer provided more conducting pathways for electrons. Therefore, the mobility of SIZO TFTs was increased.¹⁶ Also, because of this result, increase of on-current was observed with the increase of In ratio. In previous reports, mobility is enhanced by increasing the carrier concentration in IZO²⁰ and IGZO.²¹ The carrier concentration was calculated by the following formulas

$$N_{cp} = \frac{C_i V_{on}}{qt_c}$$

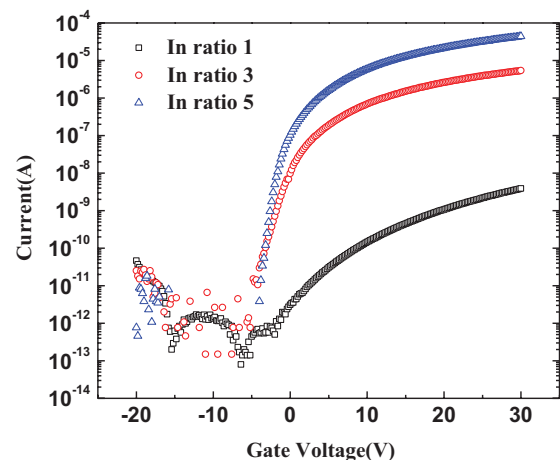


Figure 4. Drain current versus gate-voltage transfer characteristics of solution-processed SIZO TFTs as a function of indium molar ratio.

Table I. Comparison of the electrical parameters including V_{th} , Ion/off, μ_{FE} , S.S, and rms roughness for solution processed SIZO TFTs with different indium molar ratio.

In ratio (anneal 250°C)	V_{th} (V)	On/off ratio	μ_{FE} (cm ² /V s)	S.S (V/decade)	Carrier concentration (numbers/cm ³)
In ratio 1	4.37	2.35×10^3	5.04×10^{-5}	7.69	8.55×10^{16}
In ratio 3	-0.59	5.07×10^5	0.63	1.22	1.19×10^{17}
In ratio 5	-0.75	1.14×10^7	4.59	0.80	2.14×10^{17}

where C_i , q , and t_c are the gate dielectrics capacitance per area, elementary charge, and the active channel layer thickness, respectively.²²

Table I summarizes electrical parameters of the SIZO solution TFTs and surface roughness as a function of the In molar ratio. The subthreshold swing (S.S) value of TFTs decreases possibly related with surface roughness as increasing In ratio. S.S value was influenced by interface trap density at the interface between the active channel layer and the gate insulator with surface morphology. The surface morphology of SIZO films with more In contents became more smoother than that of the SIZO with a small fraction of In contents. Therefore, as the rms roughness value increases, more carriers could be trapped in defect site.¹⁷

In conclusion, we fabricated solution-processed SIZO films into active channel layer in TFTs as varying In molar ratio, and studied the effect of the chemical composition of SIZO based TFTs. We confirmed that the SIZO films annealed at 250°C were amorphous phase. The effect of varying the In contents were significant in the SIZO based TFTs. As increasing the In content, the excess In affects films formation of SIZO and leads to decrease of surface roughness. So, S.S value was improved due to the deceased interface trap density. The V_{th} was negatively shifted from 4.37 to -0.75 V by increasing carrier concentration due to increased In contents as we expected. Also the increase of the on current and the field effect mobility due to the increased carrier concentration has been clearly observed. This proposed that the characteristics of SIZO TFTs can be improved by controlling the In molar ratio in the SIZO based TFTs, and we obtained the device characteristics of optimized indium ratio in solution processed SIZO TFTs.

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