ECS Transactions, 50 (8) 101-106 (2012)
10.1149/05008.0101ecst ©The Electrochemical Society

Simple Aqueous Solution Route for Fabrication High Performance Oxide TFT

B.-S. Bae, Y. H. Hwang, J.-S. Seo, and G.-M. Choi

Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST) Daejeon 305-701, Republic of Korea

Metal oxide semiconductor attracts considerable attentions for driving circuit of next generation displays and energy devices owing to their simultaneous transparency and high electrical performance. We report fluorine doped zinc tin oxide (ZTO:F) and indium zinc oxide (IZO) thin-film transistors (TFT) via aqueous route. The aqueous route enables the fabrication of oxide TFT at low temperature with reasonable cost. The ZTO:F TFT exhibits good electrical performance and stability over electrical stress due to the effective removal of oxygen vacancy and generation of carrier by F doping. The IZO TFTs also shows good performance in terms of mobility and operation accuracy. Finally, the optimized IZO TFT is fabricated on plastic substrate with 250 ℃ annealing and the device exhibits sufficient performance for operation of various displays and basic circuitries.

Introduction

Metal oxide semiconductors (MOS) have attracted a great deal of attention as a channel layer for thin-film transistors (TFT) in display and circuitry applications (1, 2). Owing to their high mobility, good uniformity, and high transparency, oxide TFTs are considered as a most promising device for high performance and large area applications. Among MOSs, amorphous oxides based on heavy metal oxides with the $(n-1)d^{10}ns^0$ $(n\geq4)$ electronic configuration that have a large spatial spreading of the s-orbital for a considerable overlap between neighboring orbitals are promising candidates for high performance channel layer material for TFT (3). Most amorphous oxide semiconductors are generally prepared by vacuum based deposition techniques such as radio-frequency magnetron sputtering and pulse laser deposition. Many MOS, such as zinc- and indium-based oxide materials, have been reported for transparent channel layers in TFTs. They exhibited good performance in terms of mobility and on-to-off current ratios in the range of 1-50 $cm^2V^{-1}s^{-1}$ and 10^6-10^7, respectively (4, 5). These techniques, however, require costly equipment and present difficulties for economical fabrication of large area devices even at room temperature.

The solution processed thin-film deposition techniques, such as spin coating, dip coating, and roll coating, offer various benefits over vacuum based deposition techniques: simplicity, high throughput, and low cost (6, 7). They also enable direct pattering that could replace conventional photolithographic process with reasonable cost. However, the high annealing temperature for oxide formation in solution process restricts the application of it. Since metal hydroxide related species are gradually converted to the oxide through thermal annealing, the high annealing temperature is required for fabrication of oxide TFTs (8). During annealing, removal of organic residue from anion and solvent also takes place. In alcohol based precursor solution, the organic solvents have benefits in good solubility and coating property. However, the organic group requires additional thermal energy for removal and results in high process temperature. On the other hand, the aqueous route allows wide selection of precursor due to the high dielectric constant of water, over 60. Since aqueous route utilizes rapid hydrolysis and condensation reactions, it enables the low energy kinetics of M-O-M network formation without any organic residues (9).

Previously, we have fabricated the novel ZTO:F and IZO TFTs, which were activated with low temperature annealing and exhibited good performance, via aqueous route (9, 10). In this work, the detailed study of F doping effect on ZTO film for ZTO:F TFT is proceeded and IZO TFT is fabricated on plastic substrate for realization of flexible electronics.

Experiment

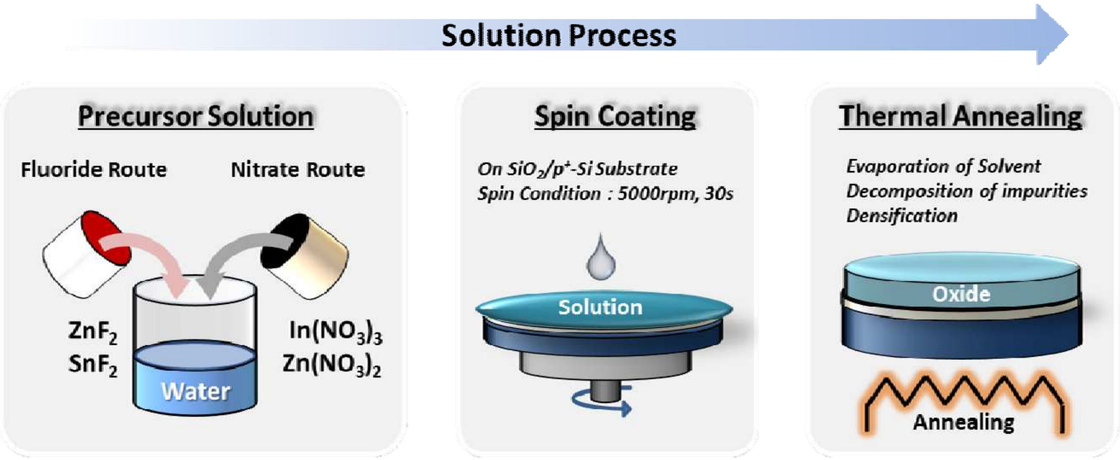

Figure 1. Experimental Procedure for Oxide Film Formation via Aqueous Route.

Preparation of Fluoride Route Solution

All reagents were purchased from Aldrich and used as received. The precursor solution for ZTO:F is prepared by dissolving zinc fluoride hydrate ($ZnF_2 \cdot H_2O$) and tin fluoride (SnF_2) in DI water, solvent. The concentration of metal precursors was 0.2 M and the molar ratio of (Sn/Sn+Zn) was 0.5.

Preparation of Nitrate Route Solution

The aqueous solution for IZO was prepared by dissolving indium nitrate ($In(NO_3)_3 \cdot xH_2O$) and zinc nitrate ($Zn(NO_3)_2 \cdot xH_2O$) in DI water. The concentration of metal precursors was 0.2 M and the molar ratio of (In/In+Zn) was 0.7.

Fabrication and Characterization of Oxide TFTs

Prior to film deposition, precursor solutions were stirred for 4 hrs at room temperature under ambient atmosphere and a clear, colorless, and homogeneous solution was obtained. The solutions were filtered through a 0.22 μm syringe filter (PTFE, GE) and spin coated at a speed of 5000 rpm atop of the SiO_2/Si substrate for 30 s. A 100nm of SiO_2 layer, which served as a gate insulator, was thermally grown on top of the heavily boron (p+) doped silicon wafer. After film deposition, the film was annealed on a hot plate at given temperature under ambient air. A bottom-gate, top-contact type structure was used for characterizing the fabricated TFTs. 100 nm aluminum source and drain electrodes were deposited by an e-beam evaporator through a shadow mask under pressure of 10^{-6} Torr. The fabricated channel length and width were 100 and 1000 μm, respectively. After the fabrication of TFTs, the performance of the devices was measured in a dark room under the ambient atmosphere using a HP 4155A semiconductor parameter analyzer.

Result and Discussion

Fluoride Route Oxide TFT

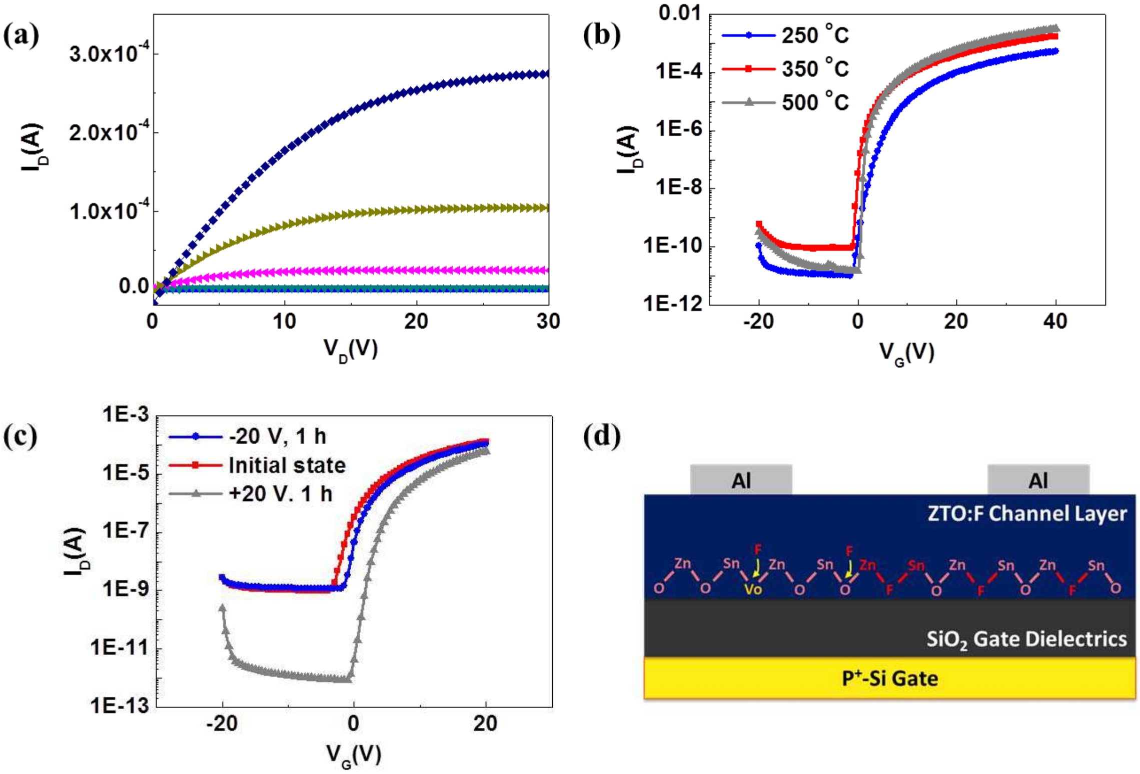

Figure 2. (a) Output characteristics of 250 ℃ annealed ZTO:F TFT. (b) Transfer characteristics of ZTO:F TFTs according to the annealing temperature. (c) Electrical stability of the 250 ℃ annealed ZTO:F TFT. (d) Scheme of cross sectional view for ZTO:F TFT (9).

The electrical performance of the ZTO:F TFTs are shown in Fig. 2 (a) and (b). The device was activated with 250 ℃ annealing (9). The electrical performances of the oxide TFTs including the saturation mobility and the threshold voltage were calculated from a linear fitting to the plot of the square root of I_D versus V_G using the following equation in the saturation region

$$I_D = \frac{WC_i}{2L}\mu(V_G - V_{th})^2 \qquad [1]$$

Here, W, C_i, μ, V_{th}, and L are the channel width, capacitance per unit area of the SiO_2 gate insulator (dielectric constant ~ 3.9), saturation mobility, threshold voltage, and channel length, respectively (11). The calculated electrical performance of the oxide TFTs are summarized in table 1. As the annealing temperature increases the performance of the TFT was improved due to the improvement of the microstructure of the thin-film (12). The electrical stability of the TFT from negative and positive bias stress was observed, shown in Fig. 2 (c). The device exhibited good resistance over electrical stress, compared to the previous reports. Since the fluorine doping on ZTO decreases the oxygen vacancy, the TFT shows good stability to the electrical stress (9). In addition, the substitution of F into O state generates extra free carrier, which contributes the conduction, and improves the electrical performance of the device.

Aqueous Route Oxide TFT

The output and transfer characteristics of IZO TFTs are displayed in Fig. 3 (10). The TFT was activated with low temperature annealing due to the unique structure in the precursor solution states. The unique structure allows both low temperature decomposition and good storage stability, which is the important aspect in sol-gel chemistry (10). As the annealing temperature increases, the interface between gate insulator and semiconductor is improved and charge carriers are generated. The increased number of charge carrier shifts the transfer curve to the negative voltage.

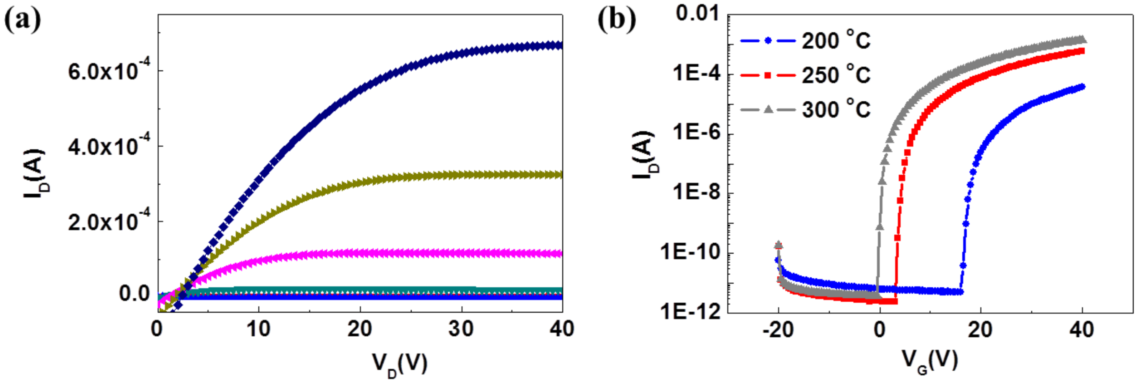

Figure 3. (a) Output characteristics of 250 ℃ annealed IZO TFT. (b) Transfer characteristics of IZO TFTs according to the annealing temperature (10).

In solution processed oxide TFT, the hydroxide related species are gradually converted to the oxide through thermal annealing. However, the high temperature for sufficient conversion restricts the realization of oxide TFT on plastic substrate. The aqueous route decreases the process temperature by formation of metal-aquo structure and activates the oxide TFT even with 200 ℃ (10). For the convenience of process, the

PI substrate was laminated on the carrier glass using cool-off-type adhesive (Intelimer) for glass like process. The 150 nm thick In-Sn-O (ITO) gate electrode was deposited at room temperature by RF magnetron sputtering. The Al_2O3 gate dielectric was prepared by atomic layer deposition technique at 150 ℃ for 176 nm using trimethyl aluminum and water as an Al source and oxygen precursors, respectively. The ITO source and drain electrode of 150 nm were grown using RF magnetron sputtering at room temperature. The structure of IZO TFT on PI substrate is illustrated in Fig. 4 (a). The electrical performance IZO TFT, which is fabricated on PI substrate, is shown in Fig. 4 (c) and (d). The TFT was operated with low gate voltage, even at 0.5 V, and exhibited good electrical performance of mobility over 4 $cm^2V^{-1}s^{-1}$, which is a sufficient characteristic for display and basic circuitry applications (10). The detailed performances are listed in table 1.

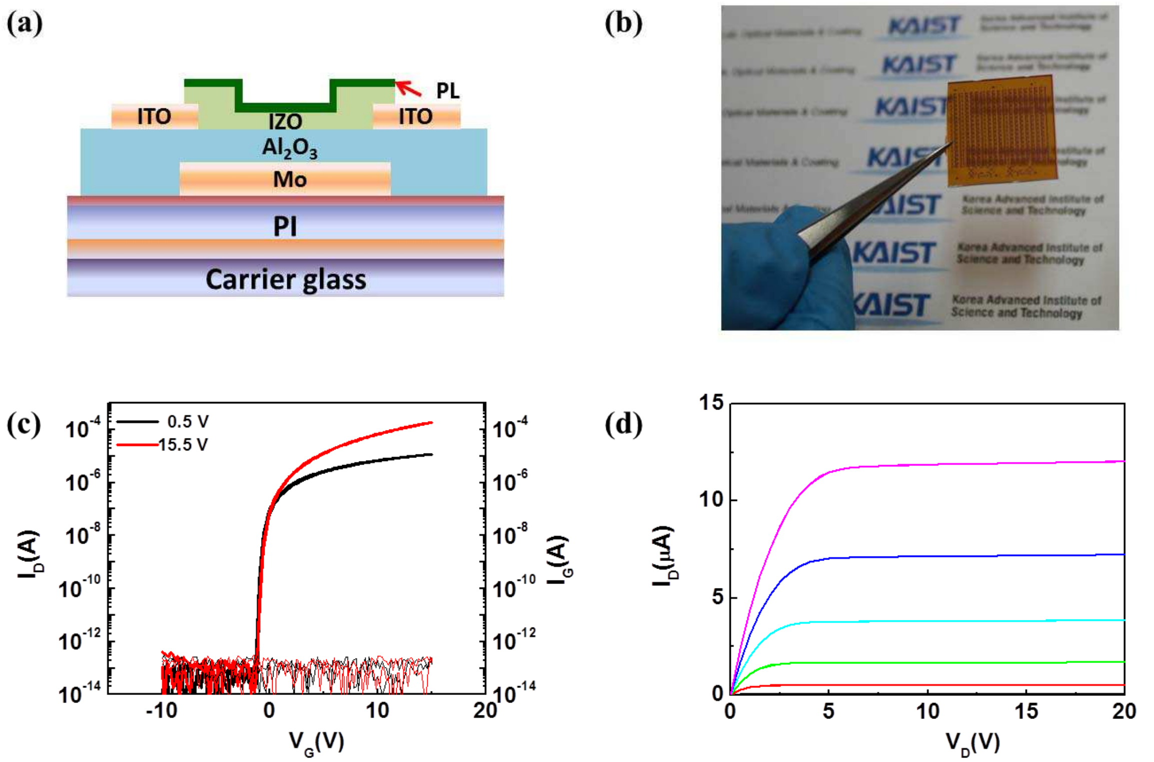

Figure 4. (a) Scheme of cross sectional view, (b) photo image, (c) transfer characteristics, and (d) output characteristics for IZO TFT on PI substrate (10).

TABLE I. Performance of Aqueous Solution Processed Oxide TFTs.

Material	Temperature	Mobility	Ion/Ooff	S.S.
ZTO:F	250 ℃	2.85 $cm^2V^{-1}s^{-1}$	> 10^7	0.87
ZTO:F	350 ℃	7.93 $cm^2V^{-1}s^{-1}$	> 10^7	0.67
ZTO:F	500 ℃	15.02 $cm^2V^{-1}s^{-1}$	> 10^8	0.19
IZO	200 ℃	0.61 $cm^2V^{-1}s^{-1}$	> 10^6	0.32
IZO	250 ℃	3.84 $cm^2V^{-1}s^{-1}$	> 10^7	0.27
IZO	300 ℃	7.41 $cm^2V^{-1}s^{-1}$	> 10^8	0.22

IZO (PI sub.)	250 ℃	4.03 $cm^2V^{-1}s^{-1}$	> 10^8	0.12

Conclusion

The aqueous route allows both the fabrication of oxide TFT at low temperature and high performance oxide TFTs. The ZTO:F TFT was activated with low temperature annealing, as low as 250 ℃ annealing and exhibited good mobility, over 2.5 $cm^2V^{-1}s^{-1}$. As annealing temperature increased, the performance of the ZTO:F was also improved and showed mobility over 15 $cm^2V^{-1}s^{-1}$, with 500 ℃ annealing. The IZO TFT was fabricated on plastic substrate with 250 ℃ annealing and exhibited good performance in terms of mobility (> 4 $cm^2V^{-1}s^{-1}$) and on-to-off current ratio (>10^8).

Acknowledgments

This work was supported by the Materials Original Technology Program (10041222) funded by the Ministry of Knowledge Economy (MKE, Korea). This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST)(CAFDC- 20120000822).

References

1. K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, and H. Hosono, Nature (London) **432**, 488 (2004).
2. E. Fortunato, P. Barquinha, A. Pimentel, A. Goncalves, A. Marques, L. Pereira, and R. Martins Adv. Mater (Weinheim Ger) **17**, 590 (2005).
3. T. Kamiya and H. Hosono, NPG Asia Mater., **2**, 15, (2010).
4. H.Q. Chiang, J.F. Wager, R.L. Hoffman, J. Jeong, and D.A. Keszler, Appl. Phys. Lett., **86**, 013503 (2005).
5. G. O. T. Kamiya, K. Nomura, and H. Hosono, Sci. Technol. Adv. Mater., **11**, 1, (2010).
6. A. C. Arias, J. D. MacKenzie, I. McCulloch, J. Rivnay, and A. Salleo, Chem. Rev., **110**, 3 (2010).
7. Y. H. Hwang, J. H. Jeon, S.-J. Seo, and B.-S. Bae, Electrochem. Solid-State Lett., **12**, H336 (2009).
8. C.J. Brinker and G.W. Scherer: Sol–Gel Science (Academic Press, Boston), p. 42 (1990).
9. J-H. Jeon, Y. H. Hwang, J. Jin, and B.-S. Bae, MRS Communications, **2**, 17 (2012).
10. Y. H. Hwang, J.-S. Seo, J. M. Yun, H. Park, S. Yang, S.-H. K. Park, and B.-S. Bae, NPG Asia Mater., submitted.
11. R. A. Street, Adv. Mater., **21**, 2007 (2009).