

Reduction of Oxygen Vacancy and Hydroxyl Group Defects in Oxide Semiconductor by Chloroform Treatment for Short-Channel Thin-Film Transistors

Taebin Lim*, Young Jae Kim**, Jiwon Sun*, Young Duck Kim**, and Jin Jang*

*Advanced Display Research Center, Department of Information Display, Kyung Hee University, Seoul 02447, South Korea, Tel.: +82-2-961-9153, Fax: +82-2-961-9154

**Department of Physics and Department of Information Display, Kyung Hee University, Seoul, 02447, South Korea

Abstract

We report a chloroform treatment method to reduce oxygen vacancies (V_o) and hydroxyl group (-OH) defects in oxide semiconductor thin film for short channel length thin-film transistor (TFT). This method is very simple and cost-effective. The reduction of V_o and -OH group defects after chloroform treatment is confirmed by XPS measurement. We fabricated short channel coplanar c-IGTO and amorphous InGaO (a-IGO) TFTs with/without chloroform treatment. The average V_{TH} shifted from -9.9 V to -0.8 V and the average SS decreased from 0.39 to 0.33 V_{dec}^{-1} for the 0.8 μm c-IGTO TFTs. The positive bias temperature stress (PBTS) test results are excellent after treatment.

Author Keywords

Short-channel TFT; coplanar oxide TFTs; chloroform treatment; defects; crystalline InGaSnO; amorphous InGaO

1. Introduction

Oxide thin-film transistors (TFTs) have attracted considerable attention due to their potential applications in low-cost, high-performance, active-matrix organic light-emitting diode (AMOLED) display backplanes.(1,2) Among various oxide semiconductors, indium gallium oxide (IGO) and indium gallium tin oxide (IGTO) have the advantages of high mobility and excellent stability.(3-5) However, the electrical characteristics of oxide TFTs are significantly affected by defects such as oxygen vacancies (V_o) and hydroxyl (-OH) group bonding, which can make it difficult to control the carrier concentration in oxide TFTs.

To address these issues, various techniques such as thermal annealing and plasma treatments have been explored to reduce defects in oxide semiconductor films.(6,7) But they often require complex processing steps and may increase the cost of production. Therefore, finding simple and low-cost methods is crucial.

In this study, we propose a cost-effective method to reduce the defects in both crystalline IGTO (c-IGTO) and amorphous IGO (a-IGO) thin films using chloroform, a simple and cheap organic solvent. The effect of chloroform treatment on c-IGTO thin films was evaluated through X-ray photoelectron spectroscopy (XPS) analysis, which resulted in significant reduction in V_o and -OH group defects. In addition, the chloroform treatment leads to positive shift of the threshold voltage (V_{TH}) and improve the positive bias temperature stress (PBTS) of the TFTs.

The chloroform treatment can enhance the electrical performance and reliability of oxide TFT. Therefore, it can be a promising method for applications in the manufacturing of low-cost, and high yield AMOLED displays.

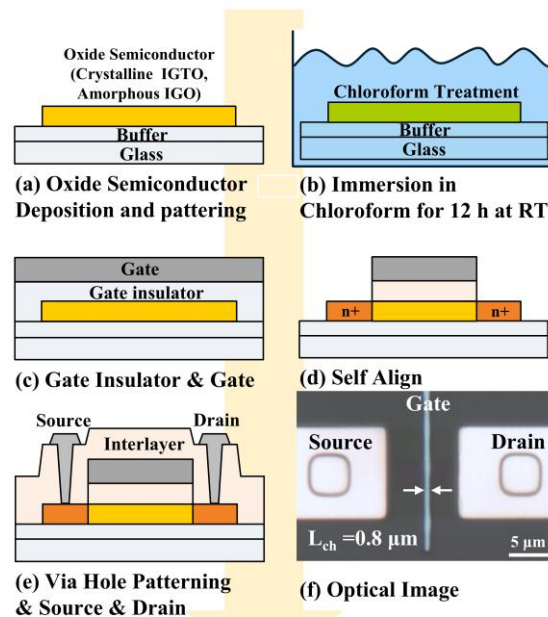


Figure 1. The fabrication process flow of a coplanar c-IGTO TFT with chloroform treatment. (a) Deposition of 6 nm amorphous IGTO film by sputtering. After that, patterning and crystallization process were conducted. (b) Chloroform treatment by immersing c-IGTO thin film in Chloroform (99.8 %) for 12 h at RT. (c) Deposition of 100 nm of SiO_2 and 100 nm of Mo for gate insulator and top gate, respectively. (d) Self-align process. Patterning of gate electrode and gate insulator and doping of n+ in source and drain region. (e) Deposition and patterning of 300 nm of SiO_2 for interlayer and 200 nm of Mo for source/drain electrode. (f) Optical image of fabricated c-IGTO TFT. The channel width and length are 4 and 0.8 μm , respectively.

2. Experimental

The IGTO thin films were deposited on a SiO_2 buffered glass substrate using a target of In 78.0 %, Ga 18.5 % and Sn of 3.5 %.(8) The IGO thin films were deposited by reactive sputtering with In 70 % and Ga 30 % target. For crystallization of IGTO, the annealing process was conducted at 500 $^{\circ}C$ for 30 min

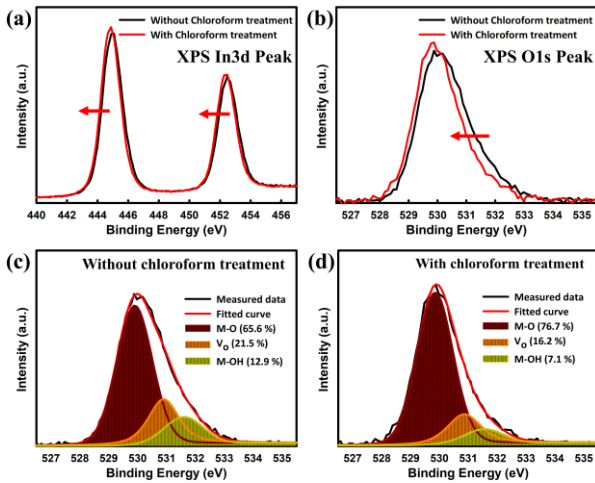


Figure 2. Comparison of XPS (a) In3d and (b) O1s peak of c-IGTO thin film without and with Chloroform treatment. Deconvoluted XPS O1s peaks of c-IGTO thin film (c) without and (d) with Chloroform treatment. Three Gaussian distributions with peaks at 529.9 ± 0.05 , 530.9 ± 0.1 , and 531.6 ± 0.2 eV, corresponding to metal-oxygen (M-O) bonds, oxygen vacancies (V_o), and metal-hydroxyl groups (M-OH), respectively.(8)

in O_2 environment. Amorphous IGO layers were annealed at 350 oC in air after deposition. The XPS (Nexsa, Thermofisher) analysis were performed on the IGTO thin films after crystallization and N_2O plasma treatment. O1s XPS spectra were deconvoluted after calibrated with a C 1s peak (284.8 eV).(9)

Fig. 1 shows the fabrication process of coplanar c-IGTO and a-IGO TFTs. First, a 100 nm SiO_2 buffer layer was deposited on a glass substrate by plasma enhanced chemical vapor deposition (PECVD) at 420 °C. The 6 nm IGTO or 10 nm of IGO layer was deposited by reactive sputtering and patterned for active island as shown in Fig. 1(a). The annealing process was carried out and N_2O plasma was conducted.(7) For the chloroform treatment, the c-IGTO and a-IGO thin films were immersed in the chloroform solution (99.8 %) for 12 h at room temperature (RT) (Fig. 1(b)). After immersion the sample in chloroform, it was cleaned in an isopropyl alcohol with ultra-sonication. Subsequently, 100 nm SiO_2 was deposited by PECVD for gate insulator (GI) and 100 nm Mo was deposited as gate electrode by reactive sputtering.(Fig. (c)) By the self-aligned process, the gate metal and GI layers were etched, and n+ doping with NF_3 plasma was carried out for formation of ohmic contact as shown in Fig. 1(d).(10) Fig. 1(e) shows the deposition of 300 nm thick SiO_2 by PECVD for interlayer dielectric, and the via holes formation for source/drain contacts. Finally, 200 nm of Mo was deposited as source/drain electrodes. Fig. 1(f) shows the optical image of fabricated c-IGTO TFT.

All electrical performances of oxide TFTs were measured by Agilent 4156C semiconductor parameter analyzer. The threshold voltage (V_{TH}) was extracted at the gate voltage (V_{GS}) corresponding to constant drain current (I_{DS}) of $W/L * 10^{-11}$ A at drain voltage (V_{DS}) of 0.1 V. The W and L are channel width and channel length, respectively. The field effect mobility (μ_{FE}) was obtained by the $(L/(W * C_{ox} * V_{DS})) * g_{m_max}$, where C_{ox} is the capacitance of the gate dielectric and g_{m_max} is the maximum transconductance. The sub-threshold swing (SS) was taken as

$(d \log(I_{DS})/dV_{GS})^{-1}$ over the range of $10 \text{ pA} \leq I_{DS} \leq 100 \text{ pA}$, with $V_{DS} = 0.1 \text{ V}$.

3. Result and Discussion

We conducted the XPS analysis to see the effect of chloroform treatment on chemical bonding in c-IGTO thin film. Fig. 2(a) shows the XPS In3d peak comparison of c-IGTO with and without chloroform treatment. The film with chloroform treatment shows a shift in the In3d peak toward lower binding energy. This indicates reduced -OH related defects after chloroform treatment. (11,12) The comparison of XPS O1s peak is shown in Fig. 2(b), which also shows the shift in the binding energy toward lower binding energy. Fig. 2(c) and (d) show the deconvoluted XPS O1s peak, deconvoluted into metal-oxygen bonding (M-O), V_o , and metal-hydroxyl group (M-OH).(8) Through chloroform treatment, M-O bonding increased from 65.6 % to 76.7 %, V_o decreased from 21.5 % to 16.2 %, and M-OH decreased from 12.9 % to 7.1 %. XPS analysis confirmed that chloroform treatment effectively reduces V_o and -OH related defects.

We fabricated the coplanar, c-IGTO and a-IGO TFTs which is illustrated in Fig. 3(a) and (d), to see the effect of chloroform treatment. Fig. 3(b) shows the comparison of transfer curves of c-IGTO TFTs with channel length of 0.8 μm , and Fig. 3(c) and Table 1 show a comparison of statistical data for V_{TH} , μ_{FE} , and SS according to chloroform treatment. V_{TH} shifted positively from -9.9 to -0.8 V, μ_{FE} decreased from 19.3 to 15.2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$, and SS decreased from 0.39 to 0.33 Vdec^{-1} . The positive shift of V_{TH} and decrease in SS occur due to the reduction of V_o and -OH related defects by chloroform treatment, which is consistent with the XPS analysis results. Fig. 3(e) and (f) show the comparison of transfer curves and TFT parameter of 2.0 μm channel length a-IGO TFTs, showing similar trend. This suggests that the short channel oxide TFT can be achieved through chloroform treatment.

Fig. 4(a) shows the hysteresis-free characteristics of the c-IGTO TFT with chloroform treatment. The hysteresis was measured by performing forward sweep followed by backward sweep of V_{GS} . There is V_{TH} difference less than 0.025 V when compared by

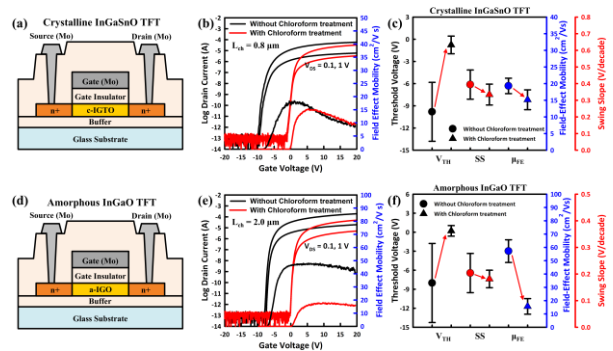


Figure 3. Electrical characteristics of coplanar c-IGTO and a-IGO TFT. (a) Schematic diagram of coplanar structured c-IGTO TFT. (d) The comparison of transfer characteristics of c-IGTO with field effect mobility (μ_{FE}). (c) Statistical data of 13 c-IGTO TFTs device performance summary including V_{TH} , μ_{FE} and SS of TFT parameters. (d) Schematic diagram of coplanar a-IGO TFT. (e) The comparison of transfer characteristics of a-IGO. (f) Statistical data of 7 a-IGO TFT parameters.

forward and backward sweeps. PBTS tests were performed at V_{GS} stress of +20 V with V_{DS} of 0 V at 60 °C, as shown in Fig. 4(b) and (c). After 500 s of bias stress, 0.6 V of V_{TH} shifted positively. This is caused by an electron trap in the interface defects with GI.(13) But after 500 s, it showed a stable behavior without change in V_{TH} . In contrast, the c-IGTO TFT without chloroform treatment shows the steady positive shift in V_{TH} due to charge trapping and defect generation during bias stress.(14) However, c-IGTO TFT with chloroform treatment can suppress defect generation.(14)

Table 1. Comparison of average TFT parameters of coplanar oxide TFTs fabricated with and without chloroform treatment.

Oxide Semiconductor	Chloroform treatment	Channel Width /Length	Avg. V_{TH} (V)	Avg. Mobility ($cm^2V^{-1}s^{-1}$)	Avg. SS (Vdec $^{-1}$)
c-IGTO	Without	4/0.8	-9.9	19.3	0.39
	With	4/0.8	-0.8	15.2	0.33
a-IGO	Without	20/2	-7.0	57.2	0.20
	With	20/2	0.2	15.7	0.18

The development of short channel coplanar oxide TFTs with excellent reliable electrical performance, highlights that chloroform treatment method can serve as a superior alternative to conventional method for reducing defects in oxide semiconductor layer. Note that chloroform treatment is a cost-efficient approach. Therefore, chloroform treatment method has great potential for low-cost, high-performance, and highly reliable TFTs for AMOLED backplanes.

The development of short channel coplanar oxide TFTs with excellent reliable electrical performance, highlights that chloroform treatment method can serve as a superior alternative to conventional method for reducing defects in oxide semiconductor layer. Note that chloroform treatment is a cost-efficient approach. Therefore, chloroform treatment method has great potential for low-cost, high-performance, and highly reliable TFTs for AMOLED backplanes.

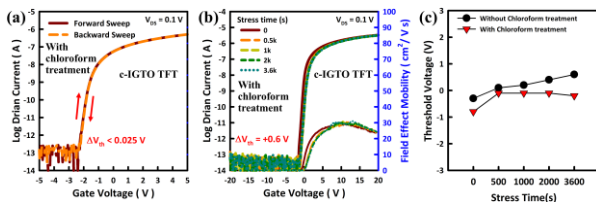


Figure 4. Stability test of c-IGTO TFTs with chloroform-treatment. (a) Hysteresis characteristics of drain current (IDS). (b) Positive bias temperature stress (PBTS) test result. For PBTS test, a +20 V of V_{GS} was applied for 1 h with $V_{DS} = 0$ V at 60 °C. (c) Comparison of V_{TH} shift during PBTS test with and without chloroform treatment.

4. Conclusions

We reported a chloroform treatment method, which is a very simple and cost-effective, to effectively reduce the oxygen vacancy and -OH related defects in oxide semiconductor thin films. The effect of chloroform treatment was evaluated by fabricating short channel coplanar oxide TFT less than 1 μ m channel length. The V_{TH} , SS and μ_{FE} of c-IGTO TFTs shifted from -9.9 V to -0.8 V, from 0.39 V/dec to 0.33 V/dec and from 19.3 $cm^2V^{-1}s^{-1}$ to 15.2 $cm^2V^{-1}s^{-1}$, respectively. In addition, the improved stability in the PBTS test (after 1 h stress, ΔV_{TH} was reduced from 0.9 V to 0.6 V) was achieved due to the reduced defects in c-IGTO thin film. In conclusion, chloroform treatment would be a good strategy for low-cost, reliable short channel oxide TFT for AMOLED TFT backplane.

5. Acknowledgements

This work was supported by the National Research Foundation of Korea(NRF) grant funded by the Korea government(Ministry of Science and ICT)(No. RS-2023-00302130).

6. References

- Bae J, Ali A, Jang J. Spray Pyrolyzed Amorphous InGaZnO for High Performance, Self-Aligned Coplanar Thin-Film Transistor Backplanes. Adv Mater Technol. 2022;2200726.
- Kim T, Choi CH, Hur JS, Ha D, Kuh BJ, Kim Y et al. Progress, Challenges, and Opportunities in Oxide Semiconductor Devices: A Key Building Block for Applications Ranging from Display Backplanes to 3D Integrated Semiconductor Chips. Advanced Materials. 2023;35(43).
- Lee J, Kim D, Lee S, Cho J, Park H, Jang J. High Field Effect Mobility, Amorphous In-Ga-Sn-O Thin-Film Transistor With No Effect of Negative Bias Illumination Stress. IEEE Electron Device Letters. 2019;40(9):1443-1446.
- Rabbi MH, Lee S, Sasaki D, Kawashima E, Tsuruma Y, Jang J. Polycrystalline InGaO Thin-Film Transistors with Coplanar Structure Exhibiting Average Mobility of ≈ 78 $cm^2 V^{-1} s^{-1}$ and Excellent Stability for Replacing Current Poly-Si Thin-Film Transistors for Organic Light-Emitting Diode Displays. Small Methods 2022; 6(9)
- Lim T, Priyadarshi S, Lee S, Sun J, Kim J, Kim B, et al. Thermally Stable InGaSnO Thin-Film Transistors Using Crystalline Oxide Semiconductor. IEEE Trans Electron Devices [Internet]. 2025;1–9. Available from: 10.1109/TED.2025.3546600
- Jeong M, Kim J, Bae J, Moadul Islam M, Lee J, Nahar S, et al. Generation of InGaZnO Nanoparticle by Ar/O₂ Plasma Exposure for Performance Improvement of Oxide TFTs. IEEE Trans Electron Devices. 2024;71(7):4160-4165.
- Rabbi MH, Billah MM, Siddik AB, Lee S, Lee J, Jang J. Extremely Stable Dual Gate Coplanar Amorphous InGaZnO Thin Film Transistor with Split Active Layer by N₂O Annealing. IEEE Electron Device Letters. 2020;41(12):1782-1785.
- Lim T, Lee S, Lee J, Choi H, Jung B, Baek S, et al. Artificial Synapse Based on Oxygen Vacancy Migration in Ferroelectric-Like C-Axis-Aligned Crystalline

- InGaSnO Semiconductor Thin-Film Transistors for Highly Integrated Neuromorphic Electronics. *Adv Funct Mater.* 2022;2212367.
9. Fang D, He F, Xie J, Xue L. Calibration of Binding Energy Positions with C1s for XPS Results. *Journal Wuhan University of Technology, Materials Science Edition.* 2020;35(4):711-718
 10. Jeong DY, Chang Y, Yoon WG, Do Y, Jang J. Low-Temperature Polysilicon Oxide Thin-Film Transistors with Coplanar Structure Using Six Photomask Steps Demonstrating High Inverter Gain of 264 V V⁻¹. *Adv Eng Mater.* 2020;22(4).
 11. Wissink T, Van De Poll RCJ, Figueiredo MC, Hensen EJM. Stability of In₂O₃nanoparticles in PTFE-containing gas diffusion electrodes for CO₂electroreduction to formate. *Journal of CO₂ Utilization.* 2023;67.
 12. Noh HY, Lee WG, G. R H, Cha JH, Kim JS, Yun WS, et al. Hydrogen diffusion and its electrical properties variation as a function of the IGZO stacking structure. *Sci Rep.* 2022;12(1).
 13. Okamoto N, Wang X, Morita K, Kato Y, Alom MM, Magari Y, et al. Uniformity and Reliability of Enhancement-mode Polycrystalline Indium Oxide Thin Film Transistors formed by Solid-phase Crystallization. *IEEE Electron Device Letters.* Published online 2024.
 14. Hong H, Kim MJ, Yi DJ, Shin DY, Moon YK, Son KS, et al. Quantitative Dynamic Evolution of Unoccupied States in Hydrogen Diffused InGaZnSnO TFT under Positive Bias Temperature Stress. *ACS Appl Electron Mater.* 2024;6(10):7584-7590.