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Effect of Post Treatment For Cu-Cr Source/Drain Electrodes on a-IGZO TFTs

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Abstract: We report a high-performance amorphous Indium-Gallium-Zinc-Oxide (a-IGZO) thin-film transistor (TFT) with new copper-chromium (Cu-Cr) alloy source/drain electrodes. The TFT shows a high mobility of $39.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ a turn-on voltage of -0.8 V and a low subthreshold swing of 0.47 V/decade . Cu diffusion is suppressed because pre-annealing can protect a-IGZO from damage during the electrode sputtering and reduce the copper diffusion paths by making film denser. Due to the interaction of Cr with a-IGZO, the carrier concentration of a-IGZO, which is responsible for high mobility, rises.

Keywords: interfaces; semiconductors; a-IGZO; Cu-Cr; TFTs; electrodes

1. Introduction

The growing demands of high resolution ($\geq 8 \text{ K}$), fast frame rate ($\geq 480 \text{ Hz}$) and large panel size ($\geq 110 \text{ inch}$) for flat panel displays need a thin-film transistor (TFT) array with high mobility and low resistance-capacitance (RC) delay [1,2]. Commercial display panels can utilize amorphous Indium-Gallium-Zinc-Oxide (a-IGZO) thin-film transistors (TFTs) to meet the high mobility requirement [3]. The replacement of conventional aluminum bus line by copper (Cu) bus line is urgent because the former's low resistivity can adequately decrease RC delay to avoid image distortion and shading [4,5]. However, there are many reports that suggest that the inter-diffusion between Cu and a-IGZO deteriorate the electrical performance [6–8]. Meanwhile, pure Cu films exhibit poor adhesion to many substrates, such as glass and SiO_2 [9–11]. Some papers use a barrier layer such as Ta, Ti, and Mo to prevent copper diffusing into IGZO and enhance the adhesion strength [12–14]. However, these technologies will increase manufacturing cost and difficulty of patterning because the etch rate of Cu and barrier layer metal (Ta, Ti, Mo, etc.) have an impact.

In this paper, we investigate the effect of copper-chromium (Cu-Cr) alloy source/drain electrodes (S/D). The introduction of Cr enhances the mobility to $39.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ which is 6 times higher than that of the TFT with no post treatment. The improvement can be attributed to the suppression of

copper diffusion, and the interaction between Cr and IGZO. Meanwhile, Cu-Cr film exhibits good adhesion with glass.

2. Experiments

The bottom-gate top-contact a-IGZO based TFTs were prepared on a glass substrate, as shown in Figure 1. A 200-nm-thick Al layer was deposited by DC magnetron sputtering as the gate electrode, then patterned by wet etching. Subsequently, a gate insulator layer of 200 nm-thick Al_2O_3 film formed on the surface of the Al by anodizing in an electrolyte consisting of 3.68 wt % ammonium tartrate solution and ethylene glycol [15]. Next, an 18 nm thick a-IGZO film was deposited by RF magnetron sputtering and patterned through the shadow mask. After the deposition, the devices were annealed at 400 °C for 1 h in air. An alloy layer of 200 nm thick Cu-Cr film as source/drain (S/D) electrodes was prepared by DC magnetron sputtering using a Cu-Cr target (Cu-0.45 wt % Cr), and patterned through a shadow mask. Finally, the devices suffered a post annealing of 300 °C for 1 h under argon (Ar) ambient.

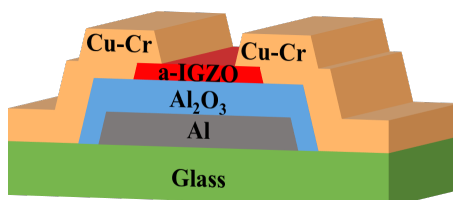


Figure 1. Schematic cross-sectional image of the amorphous Indium-Gallium-Zinc-Oxide (a-IGZO) thin-film transistors (TFTs).

3. Results and Discussion

For evaluating the adhesion strength of Cu-Cr and pure Cu films on glass, a tape test is applied to these films [16]. The pure Cu samples are totally removed from the glass while the Cu-Cr films exhibit good adhesion which remains 100% on the glass, as shown in Figure 2. Because of the low solubility for Cr in Cu (0.8% at 1075 °C), annealing can be expected to have Cr precipitates at the interface and form CrO_x to enhance the adhesion.

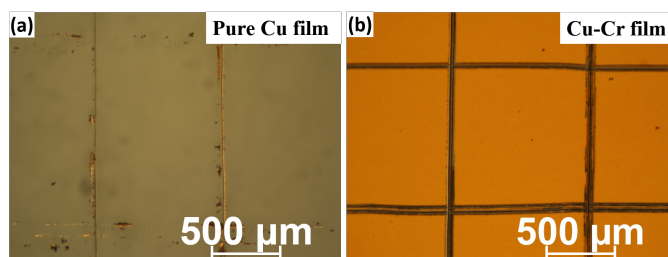


Figure 2. (a) Pure copper (Cu) and (b) copper-chromium (Cu-Cr) film image after tape test.

The transfer curves of TFTs with Cu-Cr electrodes were measured under the drain voltage of 10.1 V, as presented in Figure 3a. The TFT parameters are extracted from it. The TFT with post treatment shows a high saturated mobility (μ_{sat}) of $39.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, a subthreshold swing (SS) of 0.47 V/decade and a turn-on voltage (V_{on}) of -0.8 V . Meanwhile, the TFT without post annealing shows a μ_{sat} of $6.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, an SS of 0.26 V/decade and a V_{on} of 1.4 V. The mobility of TFT with post annealing exhibits a significant improvement compared with the previous report which shows a mobility of $16 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [4]. The contact resistance (R_c) of TFTs was extracted by transmission line method, as shown in Figure 3b. The R_c value of the Cu-Cr alloy electrodes device with post treatment is lower

than that of the device without post treatment. Therefore, the higher mobility may result from the lower R_c .

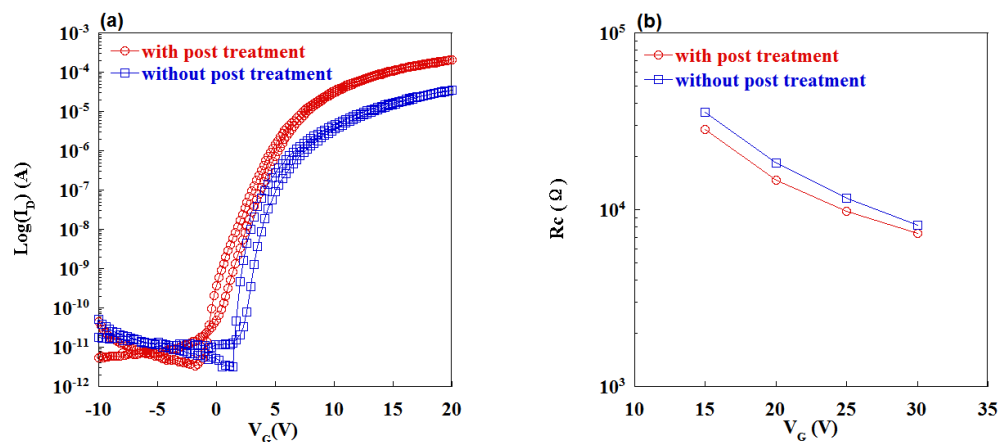


Figure 3. (a) Transfer curves and (b) variations of contact resistance for a-IGZO TFTs with Cu-Cr source/drain (S/D) electrodes.

According to previous reports, Cu atoms diffused into the channel layer would degrade the TFT performance [6–8]. However, in our TFT, the device shows excellent performance. In order to calculate the improvement, a focused ion beam transmission electron microscope (FIB-TEM) is utilized to analyze the interface of Cu-Cr and IGZO. We can observe a smooth interface at Cu-Cr S/D and a-IGZO layer, which indicates that the deposition of Cu-Cr S/D did not damage the a-IGZO film, shown in Figure 4a. In Figure 4b, it is clear that the signal of Cu element is exactly limited on the S/D side, which indicates no diffusion of Cu. According to the X-ray reflectivity curves for the a-IGZO film before and after suffering pre-annealing shown in Figure 4c, it is clear that the critical angle of a-IGZO film with pre-annealing is larger than those that are as-deposited. This indicates that the pre-annealing process makes a-IGZO film denser than as-deposited film. Therefore, we can conclude that the prevention of Cu diffusion results from the pre-annealing process, which can efficiently protect the a-IGZO layer from damage during the subsequent deposition of the Cu-Cr electrode and decrease the diffusion paths of the Cu ion.

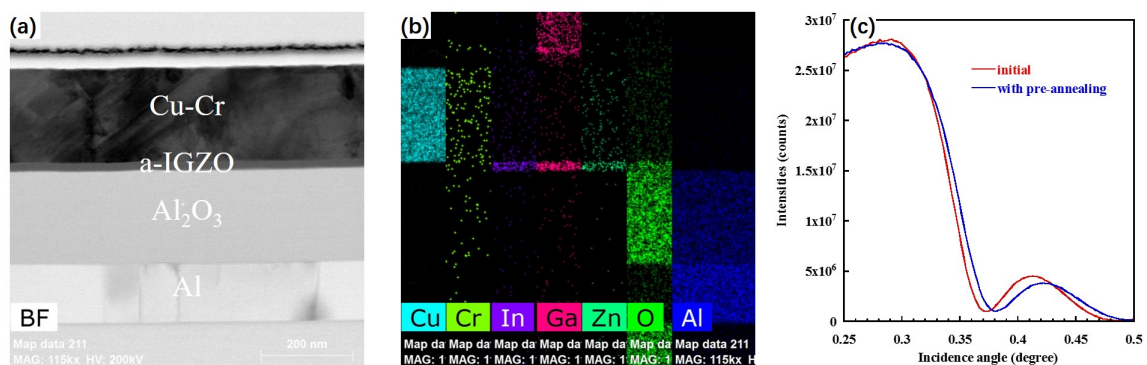


Figure 4. (a) Cross-sectional high resolution transmission electron microscope (HRTEM) image for a-IGZO TFT; (b) Cu, Cr, In, Ga, Zn, O and Al distribution detected by Energy-dispersive X-ray spectroscopy (EDS) mapping scan; (c) X-ray reflectivity (XRR) curves for a-IGZO film before and after suffering pre-annealing.

To further elucidate the interaction between a-IGZO and Cu electrode doping into Cr, the XPS depth profile of the sample with Cu-Cr/a-IGZO structure was carried out. In the experiment,

a sample of Cu-Cr (30 nm)/a-IGZO (18 nm) films was prepared on glass by DC and RF magnetron sputtering, respectively. Notably, the sample suffered the same annealing process which includes pre-annealing (400 °C for 1 h in air) after the deposition of a-IGZO and post-annealing (300 °C for 1 h in Ar ambient). Figure 5 shows core In3d and Cr2p level spectra of XPS depth profiles obtained from the Cu-Cr layer to a-IGZO layer regions. In the In3d spectra, a series of distinct peaks with lower binding energy are observed on the side of the a-IGZO layer corresponding to the free In element which indicates more oxygen vacancies. Meanwhile, the Cr2p peak can be observed only on the side of the a-IGZO layer, as shown in Figure 5b. The Cr2p_{1/2} energies (574 to 579 eV) could be ascribable to Cr oxide. These results reveal that Cr diffused into the a-IGZO film during the post-annealing phase. Then, oxygen was consumed from the a-IGZO which increased the concentration of oxygen vacancies and produced Cr oxide and a free In element. As we know, most of the carriers in the a-IGZO film are generated by oxygen vacancies. Thus, the high mobility of TFT can be attributed to the increase of carrier concentration in a-IGZO by the interaction between Cr and a-IGZO. This interpretation is consistent with the fact that the formation enthalpy of Cr₂O₃ ($\Delta H_{Cr_2O_3} = -1139.7$ kJ/mol) is smaller than In₂O₃ ($\Delta H_{In_2O_3} = -925.8$ kJ/mol), Ga₂O₃ ($\Delta H_{Ga_2O_3} = -1089$ kJ/mol) and ZnO ($\Delta H_{ZnO} = -350.5$ kJ/mol) [17]. The part-formation of Cr oxide acts as defect sites which lead to a larger SS.

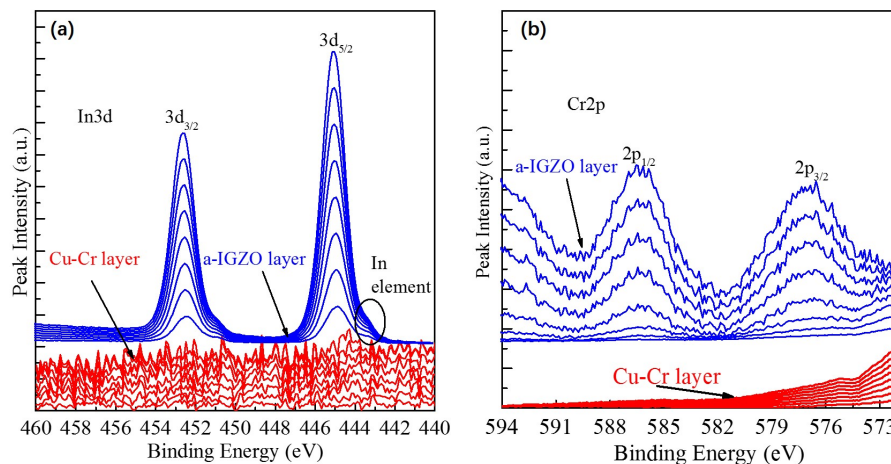


Figure 5. In3d (a) and Cr2p (b) level spectra of XPS depth profiles obtained from the Cu-Cr layer to a-IGZO layer regions.

4. Conclusions

In conclusion, we revealed the effect of Cr doping into Cu S/D electrodes on the performance of the TFT. The new Cu-Cr alloy contacted device shows a μ_{sat} of $39.4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, an SS of 0.47 V/decade and a V_{on} of -0.8 V . Cu diffusion is suppressed because pre-annealing can protect a-IGZO from damage during the electrode sputtering and reduce the copper diffusion paths by making film denser. Due to the interaction of Cr to a-IGZO, the carrier concentration of a-IGZO rises, which enhances the electrical performance of TFT. Therefore, Cu-Cr Alloy S/D electrodes are a promising approach to achieve high-performance a-IGZO TFTs.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Liao, Y.; Shao, X.; Du, Y.; Song, Y.; Hu, W.; Zhang, Z.; Chen, Y.; Wang, Y.; Ma, Q.; Yoon, D.; et al. Development of a 120 Hz 110" ultra-high-definition a-Si liquid crystal display panel. *J. Inf. Disp.* **2014**, *15*, 77–80.
2. Nathan, A.; Lee, S.; Jeon, S.; Robertson, J. Amorphous Oxide Semiconductor TFTs for Displays and Imaging. *J. Disp. Technol.* **2014**, *10*, 917–927.
3. Matsuo, T.; Mori, S.; Ban, A.; Imaya, A. 8.3: Invited Paper: Advantages of IGZO Oxide Semiconductor. *SID Symp. Dig. Tech. Pap.* **2014**, *45*, 83–86.
4. Lee, S.H.; Oh, D.J.; Hwang, A.Y.; Han, D.S.; Kim, S.; Jeong, J.K.; Park, J.W. Improvement in Device Performance of a-InGaZnO Transistors by Introduction of Ca-Doped Cu Source/Drain Electrode. *IEEE Electron Device Lett.* **2015**, *36*, 802–804.
5. Zhao, M.; Xu, M.; Ning, H.; Xu, R.; Zou, J.; Tao, H.; Wang, L.; Peng, J. Method for Fabricating Amorphous Indium-Zinc-Oxide Thin-Film Transistors With Copper Source and Drain Electrodes. *IEEE Electron Device Lett.* **2015**, *36*, 342–344.
6. Jeong, J.; Lee, G.J.; Kim, J.; Choi, B. Electrical characterization of a-InGaZnO thin-film transistors with Cu source/drain electrodes. *Appl. Phys. Lett.* **2012**, *100*, doi:10.1063/1.3694273.
7. Tai, Y.H.; Chiu, H.L.; Chou, L.S. The deterioration of a-IGZO TFTs owing to the copper diffusion after the process of the source/drain metal formation. *J. Electrochem. Soc.* **2012**, *159*, J200–J203.
8. Yim, J.R.; Jung, S.Y.; Yeon, H.W.; Kwon, J.Y.; Lee, Y.J.; Lee, J.H.; Joo, Y.C. Effects of Metal Electrode on the Electrical Performance of Amorphous In-Ga-Zn-O Thin Film Transistor. *Jpn. J. Appl. Phys.* **2012**, *51*, doi:10.1143/JJAP.51.011401.
9. Fisher, I.; Eizenberg, M. Copper ion diffusion in porous and nonporous SiO₂-based dielectrics using bias thermal stress and thermal stress tests. *Thin Solid Films* **2008**, *516*, 4111–4121.
10. Nagao, K.; Neaton, J.B.; Ashcroft, N.W. First-principles study of adhesion at Cu/SiO₂ interfaces. *Phys. Rev. B* **2003**, *68*, doi:10.1103/PhysRevB.68.125403.
11. Shan, T.R.; Devine, B.D.; Phillpot, S.R.; Sinnott, S.B. Molecular dynamics study of the adhesion of Cu/SiO₂ interfaces using a variable-charge interatomic potential. *Phys. Rev. B* **2011**, *83*, doi:10.1103/PhysRevB.83.115327.
12. Cao, Z.H.; Hu, K.; Meng, X.K. Diffusion barrier properties of amorphous and nanocrystalline Ta films for Cu interconnects. *J. Appl. Phys.* **2009**, *106*, doi:10.1063/1.3266164.
13. Park, J.S.; Kim, T.S.; Son, K.S.; Lee, E.; Jung, J.S.; Lee, K.H.; Maeng, W.J.; Kim, H.S.; Kim, E.S.; Park, K.B.; et al. Ti/Cu bilayer electrodes for SiN_x-passivated Hf-In-Zn-O thin film transistors: Device performance and contact resistance. *Appl. Phys. Lett.* **2010**, *97*, doi:10.1063/1.3505151.
14. Ning, H.-L.; Hu, S.-B.; Zhu, F.; Yao, R.-H.; Xu, M.; Zou, J.-H.; Tao, H.; Xu, R.-X.; Xu, H.; Wang, L.; et al. Improved performance of the amorphous indium-gallium-zinc oxide thin film transistor with Cu-Mo source/drain electrode. *Acta Phys. Sin.* **2015**, *64*, doi:10.7498/aps.64.126103.
15. Lan, L.; Xu, M.; Peng, J.; Xu, H.; Li, M.; Luo, D.; Zou, J.; Tao, H.; Wang, L.; Yao, R. Influence of source and drain contacts on the properties of the indium-zinc oxide thin-film transistors based on anodic aluminum oxide gate dielectrics. *J. Appl. Phys.* **2011**, *110*, doi:10.1063/1.3660791.
16. ASTM D3359-97. *Standard Test Methods for Measuring Adhesion by Tape Test*; ASTM International: West Conshohocken, PA, USA, 1997, doi:10.1520/D3359-97.
17. Haynes, W.M. *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, USA, 2014.



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