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The Origin of the High Off-State Current in p-Type Cu_2O Thin Film Transistors

Sanggil Han and Andrew J. Flewitt

***Abstract*—There is a need for a good quality p-type accumulation-mode thin film transistor (TFT) using a metal oxide semiconducting channel. P-type cuprous oxide (Cu_2O) has been proposed as a suitable semiconductor, but such TFTs have suffered from unacceptably high off-state currents. This paper studies the main origin of this high off-state current. Capacitance-voltage (C-V) characteristics reveal the accumulation of minority carriers (electrons) in the off-state regime (i.e. for a positive gate voltage). The activation energy extracted from the temperature dependence of the drain current as a function of gate voltage shows an abrupt lowering of the activation energy and pinning of the Fermi energy in the off-state region, which is attributed to subgap states at 0.38 eV from the conduction band minimum. This suggests that an electron flow in the off-state causes the high off-state current in p-type Cu_2O TFTs and not an inability to deplete the channel of holes.**

***Index Terms*—Cuprous oxide (Cu_2O), off-state current, p-type metal oxide, sputtering, thin film transistors (TFTs).**

I. Introduction

Research on p-type metal oxide thin film transistors (TFTs) is required in order to realize metal oxide-based CMOS circuits which enable low power consumption large-area electronics [1]. Cuprous oxide (Cu_2O) has been one of the promising candidates as an active layer for p-type metal oxide TFTs. This is because, contrary to most metal oxides having strongly localized O 2*p* orbitals at the valence band maximum (VBM), Cu_2O has a unique orbital configuration resulting from the close energy levels of the Cu 3*d* and O 2*p* orbitals, which introduces considerable covalency into the ionic metal-oxide network [2]-[5]. This leads to not only a significant decrease in the localization of holes by O 2*p* orbitals but also a large dispersion (i.e. low effective mass) near the VBM, and thus more effective carrier transport [6].

However, a high off-state current is widely observed in p-type Cu_2O TFTs, resulting in an unacceptably low current switching ratio (typically 10-10^4) [2], [5], [7]-[11]; this is much lower than the on/off current ratio exceeding 10^7 in n-type metal oxide TFTs [1]. This is holding back the development of metal oxide based large-area CMOS circuits. In this letter, we identify the main origin of the high off-state current in Cu_2O TFTs based on capacitance-voltage (C-V) characteristics and a change in the activation energy extracted from the temperature dependence of the drain current at various gate voltages.

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II. Experimental Details

To fabricate bottom-gate staggered p-type Cu_2O TFTs, Cu_2O active layers (~130 nm) were formed on a thermally-grown SiO_2 on a p^+-Si (0.01~0.02 Ω·cm) substrate by remote-plasma reactive sputtering using a high target utilization sputtering (HiTUS) system (Plasma Quest Limited) without substrate heating (see the features and a schematic diagram of HiTUS in [12]). The p^+-Si and SiO_2 (~260 nm) were used as a common gate electrode and a gate insulator, respectively. The reactive sputtering condition is same as that in our previous work [5], [13]. The as-deposited Cu_2O thin films were subsequently annealed using an Aixtron Cambridge Nanoinstruments Black Magic 2 system in vacuum (9.5×10^{-4} mbar) at 700 ℃ for 10 min (see film characteristics of the annealed Cu_2O such as an X-ray diffraction pattern and Hall measurement results in [5]). An infrared (IR) radiation pyrometer (Infratherm IGA8 plus) was used for monitoring the annealing temperature. The temperature ramp rate was 5 ℃·s^{-1} and the annealed sample was unloaded after the chamber was cooled for 20 min. Au (100 nm) was deposited on the annealed Cu_2O active layers (without an adhesion layer) as source/drain (S/D) electrodes using a thermal evaporator (Edwards E306A). The channel width-to-length ratio (*W*/*L*) is 10 with a channel length of 100 μm. Here, the active layers and S/D electrodes were patterned by a lift-off process using AZ5214E photoresist. The output and transfer characteristics and the temperature dependence of the drain current were obtained by an HP 4140B pA meter/DC voltage source in a dark box at an ambient condition.

In addition, metal-oxide-semiconductor (MOS) capacitors with a p^+-Si/SiO_2/Cu_2O structure and an Au top contact were simultaneously prepared in order to measure the low frequency (500 kHz) C-V characteristic of the Cu_2O active layer. This was measured using an Agilent B1500A semiconductor parameter analyzer at room temperature, where a voltage was applied to the p^+-Si and the Au electrode was grounded.

III. Results and Discussion

The output and transfer characteristics (Fig. 1) show that the fabricated Cu_2O TFTs exhibit clear p-channel behavior yielding an increase in the channel conductivity with an increase in the magnitude of the drain-source current (I_{DS}) for

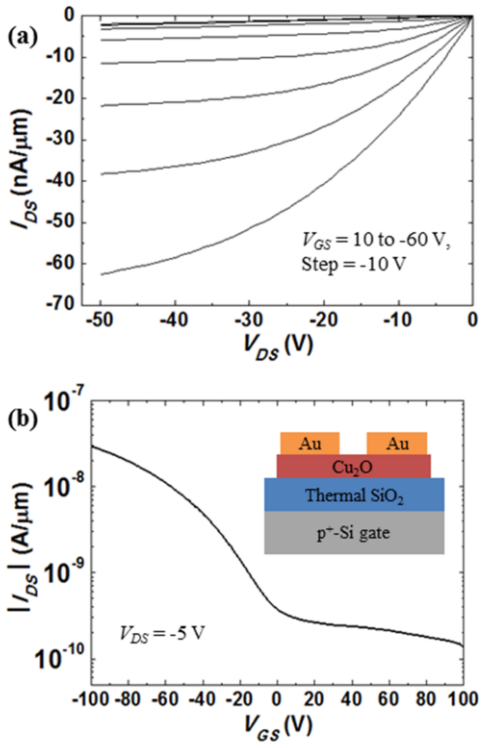

Fig. 1. (a) Output and (b) transfer characteristics of a typical fabricated Cu_2O TFT. The inset is a schematic structure of the Cu_2O TFT.

negative gate voltage (V_{GS}). However, Fig. 1 (b) shows a high off-state current and thus a low on/off current ratio (~2×10^2), which is consistent with previously-reported observations [7], [8], [10].

Figure 2 shows the C-V characteristic of the Cu_2O MOS capacitor. Contrary to n-type metal oxides such as IGZO showing only majority carrier (electron) accumulation [14], [15], interestingly, this shows that not only holes are accumulated at V_{GS} < 0 V (i.e. in the on-state region) but also electrons are accumulated at V_{GS} > 0 V (i.e. in the off-state region). Calculated results of formation energies for intrinsic defects in Cu_2O as a function of the Fermi energy (E_F) [6], [16] provide a possible interpretation of the electron accumulation.

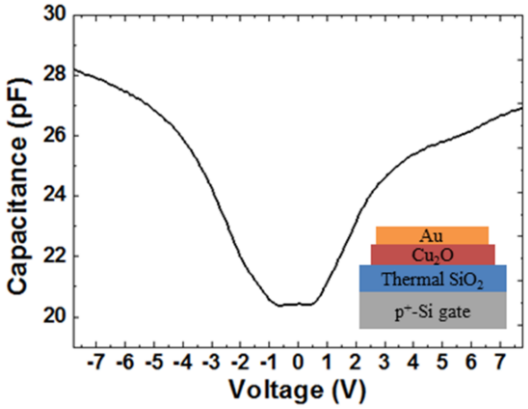

Fig. 2. The low frequency (500 kHz) C-V characteristic of a Cu_2O MOS capacitor. The inset is a schematic structure of the capacitor.

To be specific, since the main hole producer, copper vacancies (V_{Cu}), has the lowest formation energy with a small $\varepsilon(0/-)$ ionization level at E_V + 0.28 eV, Cu_2O has intrinsic p-type conductivity. However, other defects, such as oxygen vacancies (V_O) and copper interstitials (Cu_i), can act as potential donors for minority carriers (electrons) in Cu_2O. V_O do not have a charge transition level in the band gap, which means that they are only stable in the charge-neutral state and thus cannot act as donors [6], [16]. In contrast, Cu_i are amphoteric defects with both $\varepsilon(+/0)$ and $\varepsilon(0/-)$ charge transitions in the band gap; $\varepsilon(+/0)$ lies at ~1.3 eV above the VBM (i.e. Cu_i have a positive charge state Cu_i^+ when $E_F - E_V$ < 1.3 eV) [6], [16]. This means that they would act as donors for minority carriers in p-type Cu_2O, suggesting that the electron accumulation at V_{GS} > 0 V can be due to minority carriers created by Cu_i in Cu_2O.

In order to verify that electron flow is the source of the high off-state current, the activation energy (E_a) extracted from the temperature dependence of I_{DS} was investigated as a function of V_{GS}. I_{DS} is thermally activated and is described as

$$I_{DS} = I_{DS0}\exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

where I_{DS0}, k, and T are the prefactor, the Boltzmann constant and temperature [17], [18]. Here, E_a is the energy difference between E_F and either the edge of the valence band (i.e. $E_F - E_V$ for a p-type channel) or the conduction band (i.e. $E_C - E_F$ for an n-type channel). Equation (1) can be written as

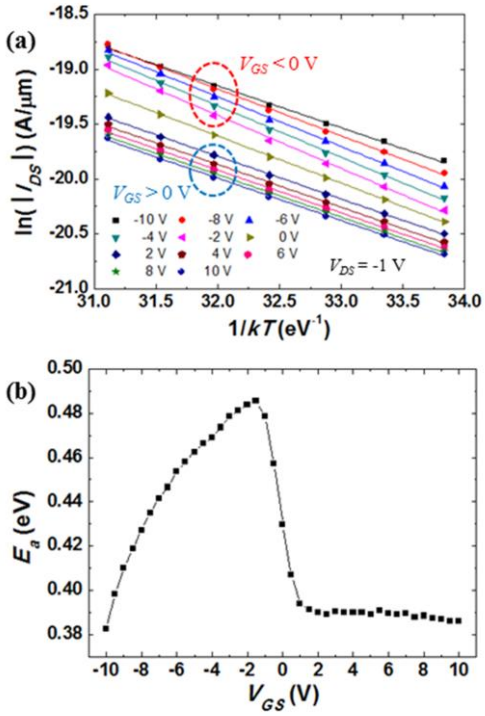

Fig. 3. (a) Temperature dependence of the drain current obtained at various V_{GS} and a fixed V_{DS} of -1 V; scatter dots are measured data and the line gradients are used for extracting the activation energy (E_a), and (b) extracted activation energy as a function of V_{GS}.

$\ln(|I_{DS}|) = (-E_a)(1/kT) + \ln(|I_{DS0}|)$, and as a result E_a can be extracted from the gradient of an $\ln(|I_{DS}|)$ versus $1/kT$ graph, as seen in Fig. 3 (a). The extracted E_a as a function of V_{GS} is shown in Fig. 3 (b). In contrast to the usual case where E_a increases in the off-state region (see the case of n-type IGZO TFTs [17]), Fig. 3 (b) shows an abrupt lowering of E_a in the off-state region. This can be understood to be due to E_F movement from near the VBM to near the conduction band minimum (CBM) based on the C-V characteristic (i.e. the channel inverts from p-type to n-type). The change in the temperature dependence of I_{DS} at V_{GS} > 0 V (i.e. an abrupt reduction in the slope, see Fig. 3 (a)) also suggests that the electron flow is the source of the high off-state current.

In addition, it is observed that E_F is not modulated by V_{GS} in the off-state region (see Fig. 3 (b)). This normally indicates pinning of the Fermi energy [19], which in this case is attributable to subgap states in the upper half of the band gap. Photoconductivity [20] and photoluminescence [21] results show that there is a subgap state at ~0.38 eV below the CBM in Cu_2O, and the authors attributed the origin of the subgap states to V_O. However, density-functional theory (DFT) analysis [16] strongly suggests that since the V_O level lies below the VBM, V_O cannot be the source of this subgap state. Although the origin of these subgap states is not certain, it is likely that it is the same states that are observed in photoconductivity and photoluminescence measurements which result in the E_F pinning observed in the TFTs in this work, and this results in the accumulation of electrons in the off-state and the high off-state current.

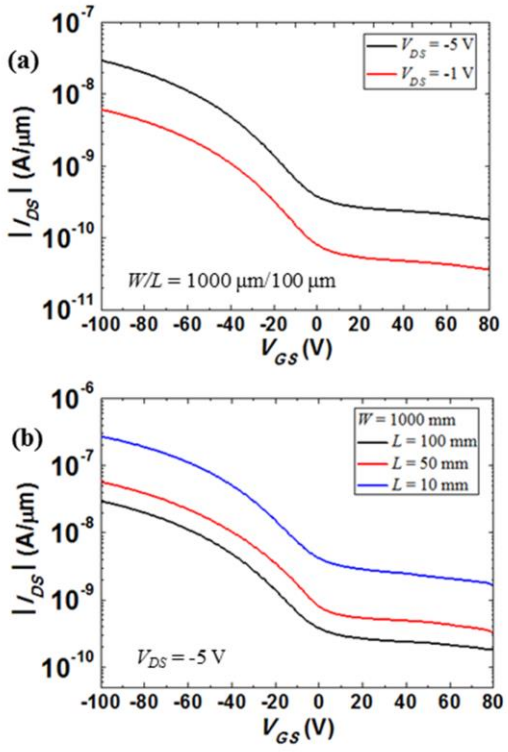

Fig. 4. Transfer characteristics as a function of (a) V_{DS} at W/L = 10, and (b) the channel width-to-length ratio (W/L) at V_{DS} = -5 V.

Figure 4 shows transfer characteristics as a function of V_{DS} and W/L. Contrary to n-type IGZO TFTs with complete channel depletion in the off-state showing no dependence of the off-state current on V_{DS} [22] and W/L [23], this shows that the off-state current increases with an increase in $|V_{DS}|$ (see Fig. 4 (a)) and a reduction in the channel length (see Fig. 4 (b)). The channel length dependence of the off-state current can be understood by a decrease in channel resistance attributable to the minority carrier (electron) accumulation with a reduction in the channel length. The dependence of the off-state current on V_{DS} and W/L provides further support for the finding that the high off-state current is due to minority carrier (electron) accumulation. This also results in significant degradation of the sub-threshold characteristic, and thus this leads to an excessively high sub-threshold slope (SS) of ~35 V/dec.

IV. Conclusion

The temperature dependence of the drain current as a function of gate voltage along with the C-V characteristics shows that minority carriers (electrons) cause the high off-state current in p-type Cu_2O TFTs, and not an inability to deplete the hole density in the channel. This electron accumulation in the off-state is considered to be due to minority carriers formed by Cu_i in Cu_2O. Based on reported results of photoconductivity and photoluminescence, pinning of the Fermi energy in the off-state could be due to the subgap states at ~0.38 eV below the CBM. Although the origin of these subgap states is not certain, reducing their density will be critical for improving the switching ratio in Cu_2O TFTs.

References

[1] E. Fortunato, P. Barquinha, and R. Martins, "Oxide semiconductor thin-film transistors: a review of recent advances," *Adv. Mater.*, vol. 24, no. 22, pp. 2945–2986, May, 2012. DOI: 10.1002/adma.201103228.

[2] E. Fortunato, V. Figueiredo, P. Barquinha, E. Elamurugu, R. Barros, G. Goncalves, S.-H. K. Park, C.-S. Hwang, and R. Martins, "Thin-film transistors based on p-type Cu_2O thin films produced at room temperature," *Appl. Phys. Lett.*, vol. 96, no. 19, p. 192102, May, 2010. DOI: 10.1063/1.3428434.

[3] H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, "Transparent p-type conducting oxides: design and fabrication of p-n heterojunctions," *MRS Bull.*, vol. 25, no. 8, pp. 28–36, Aug. 2000. DOI: 10.1557/mrs2000.148.

[4] H. Yanagi, H. Kawazoe, A. Kudo, M. Yasukawa, and H. Hosono, "Chemical design and thin film preparation of p-type conductive transparent oxides," *J. Electroceram.*, vol. 4, no. 2-3, pp. 407–414, Jun. 2000. DOI: 10.1023/A:1009959920435.

[5] S. Han, K. M. Niang, G. Rughoobur, and A. J. Flewitt, "Effects of post-deposition vacuum annealing on film characteristics of p-type Cu_2O and its impact on thin film transistor characteristics," *Appl. Phys. Lett.*, vol. 109, no. 17, p. 173502, Oct. 2016. DOI: 10.1063/1.4965848.

[6] H. Raebiger, S. Lany, and A. Zunger, "Origins of the p-type nature and cation deficiency in Cu_2O and related materials," *Phys. Rev. B*, vol. 76, no. 4, p. 045209, Jul. 2007. DOI: 10.1103/PhysRevB.76.045209.

[7] K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, "Epitaxial growth of high mobility Cu_2O thin films and applications to p-channel thin film transistor," *Appl. Phys. Lett.*, vol. 93, no. 20, p. 202107, Nov. 2008. DOI: 10.1063/1.3026539.

[8] K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, "Effects of post-annealing on (110) Cu_2O epitaxial films and origin of low mobility in Cu_2O thin-film transistor," *Phys. Status Solidi A*, vol. 206, no. 9, pp. 2192–2197, Aug. 2009. DOI: 10.1002/pssa.200881795.

[9] C.-Y. Jeong, J. Sohn, S.-H. Song, I.-T. Cho, J.-H. Lee, E.-S. Cho, and H.-I. Kwon, "Investigation of the charge transport mechanism and subgap

density of states in p-type Cu_2O thin-film transistors," *Appl. Phys. Lett.*, vol. 102, no. 8, p. 082103, Feb. 2013. DOI: 10.1063/1.4794061.

[10] S. Y. Kim, C. H. Ahn, J. H. Lee, Y. H. Kwon, S. Hwang, J. Y. Lee, and H. K. Cho, "p-channel oxide thin film transistors using solution-processed copper oxide," *ACS Appl. Mater. Interfaces*, vol. 5, no. 7, pp. 2417–2421, Mar. 2013. DOI: 10.1021/am302251s.

[11] P. Pattanasattayavong, S. Thomas, G. Adamopoulos, M. A. McLachlan, and T. D. Anthopoulos, "p-channel thin-film transistors based on spray-coated Cu_2O films," *Appl. Phys. Lett.*, vol. 102, no. 16, p. 163505, Apr. 2013. DOI: 10.1063/1.4803085.

[12] A. J. Flewitt, J. D. Dutson, P. Beecher, D. Paul, S. J. Wakeham, M. E. Vickers, C. Ducati, S. P. Speakman, W. I. Milne, and M. J. Thwaites, "Stability of thin film transistors incorporating a zinc oxide or indium zinc oxide channel deposited by a high rate sputtering process," *Semicond. Sci. Technol.*, vol. 24, no. 8, p. 085002, Jun. 2009. DOI: 10.1088/0268-1242/24/8/085002.

[13] S. Han and A. J. Flewitt, "Analysis of the conduction mechanism and copper vacancy density in p-type Cu_2O thin films," *Sci. Rep.*, vol. 7, 5766, Jul. 2017. DOI: 10.1038/s41598-017-05893-x.

[14] H. Choi, J. Lee, H. Bae, S.-J. Choi, D. H. Kim, and D. M. Kim, "Bias-dependent effective channel length for extraction of subgap DOS by capacitance–voltage characteristics in amorphous semiconductor TFTs," *IEEE Trans. Electron Devices*, vol. 62, no. 8, pp. 2689–2694, Jun. 2015. DOI: 10.1109/TED.2015.2443492.

[15] Y.-C. Tsao, T.-C. Chang, H.-M. Chen, B.-W. Chen, H.-C. Chiang, G.-F. Chen, Y.-C. Chien, Y.-H. Tai, Y.-J. Hung, S.-P. Huang, C.-Y. Yang, and W.-C. Chou, "Abnormal hump in capacitance–voltage measurements induced by ultraviolet light in a-IGZO thin-film transistors," *Appl. Phys. Lett.*, vol. 110, no. 2, p. 023501, Jan. 2017. DOI: 10.1063/1.4973856.

[16] D. O. Scanlon and G. W. Watson, "Undoped n-type Cu_2O: fact or fiction?," *J. Phys. Chem. Lett.*, vol. 1, no. 17, pp. 2582–2585, Aug. 2010. DOI: 10.1021/jz100962n.

[17] C. Chen, K. Abe, H. Kumomi, and J. Kanicki, "Density of states of a-InGaZnO from temperature-dependent field-effect studies," *IEEE Trans. Electron Devices*, vol. 56, no. 6, pp. 1177–1183, Jun. 2009. DOI: 10.1109/TED.2009.2019157.

[18] W. B. Jackson, J. M. Marshall, and M. D. Moyer, "Role of hydrogen in the formation of metastable defects in hydrogenated amorphous silicon," *Phys. Rev. B*, vol. 39, no. 2, pp. 1164–1179, Jan. 1989. DOI: 10.1103/PhysRevB.39.1164.

[19] K. Takechi, M. Nakata, T. Eguchi, H. Yamaguchi, and S. Kaneko, "Temperature-dependent transfer characteristics of amorphous $InGaZnO_4$ thin-film transistors," *Jpn. J. Appl. Phys.*, vol. 48, no. 1R, p. 011301, Jan. 2009. DOI: 10.1143/JJAP.48.011301.

[20] M. Zouaghi, B. Prevot, C. Carabatos, and M. Sieskind, "Near infrared optical and photoelectric properties of Cu_2O. III. Interpretation of experimental results," *Phys. Status Solidi A*, vol. 11, no. 2, pp. 449–460, Jun. 1972. DOI: 10.1002/pssa.2210110207.

[21] R. Garuthara and W. Siripala, "Photoluminescence characterization of polycrystalline n-type Cu_2O films," *J. Lumin.*, vol. 121, no. 1, pp. 173–178, Nov. 2006. DOI: 10.1016/j.jlumin.2005.11.010.

[22] W. Kang, C. Ahn, M. Yun, S. Cho, Y. Kim, D. Kim, B. Kim, H. Cho, and Y. Kim, "Expedient floating process for ultra-thin InGaZnO thin-film-transistors and their high bending performance," *RSC Adv.*, vol. 6, no. 68, pp. 63418–63424, Jul. 2016. DOI: 10.1039/C6RA06372A.

[23] W. Wang, L. Li, C. Lu, Y. Liu, H. Lv, G. Xu, Z. Ji, and M. Liu, "Analysis of the contact resistance in amorphous InGaZnO thin film transistors," *Appl. Phys. Lett.*, vol. 107, no. 6, p. 063504, Aug, 2015. DOI: 10.1063/1.4928626.

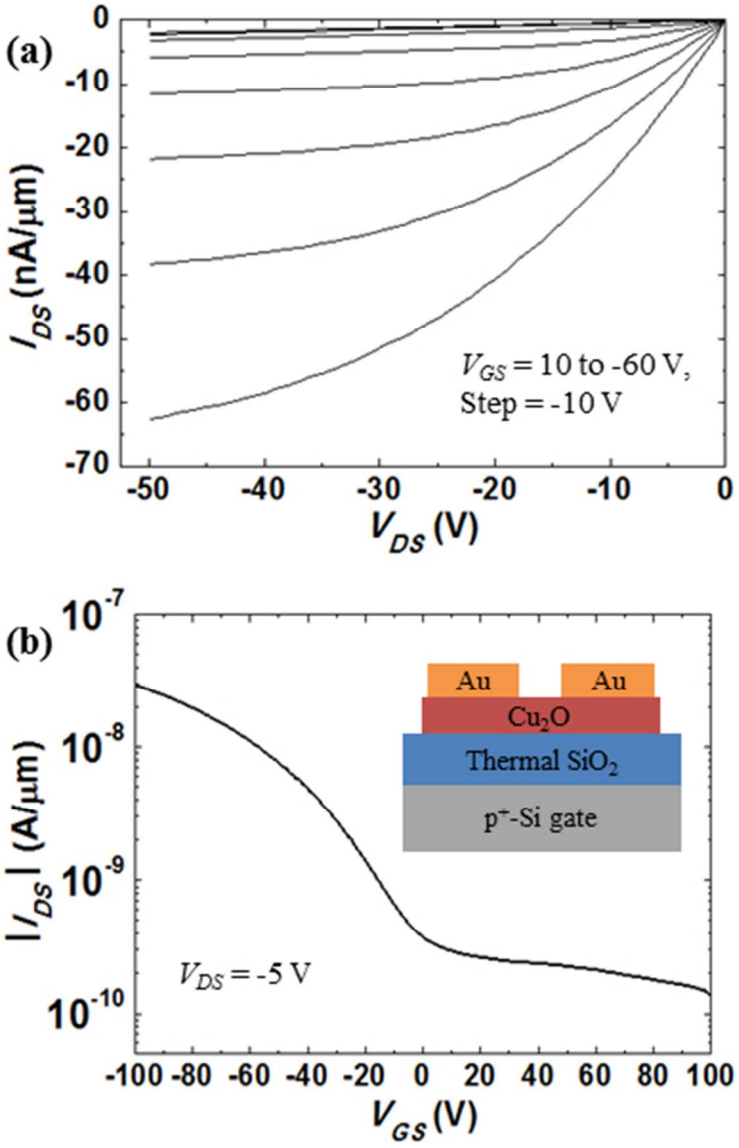

Figure 1

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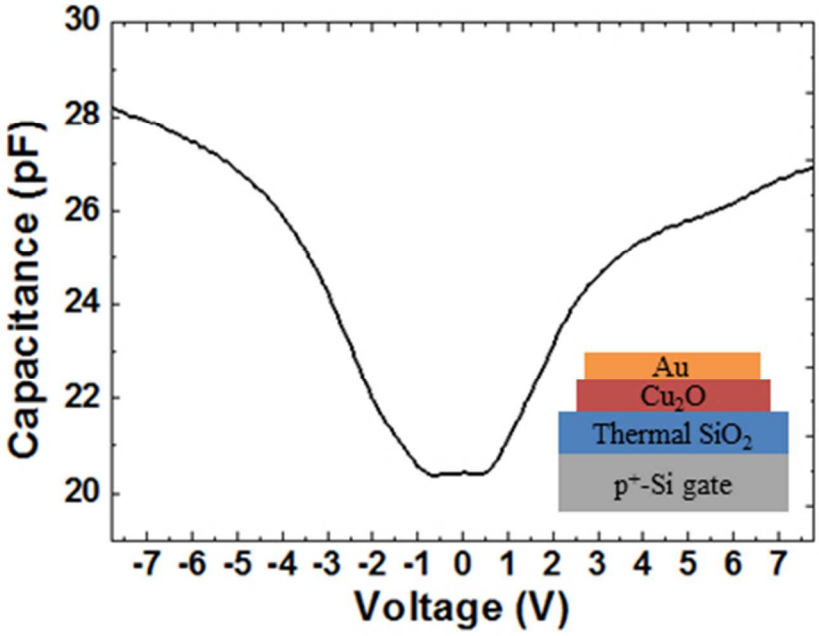

Figure 2

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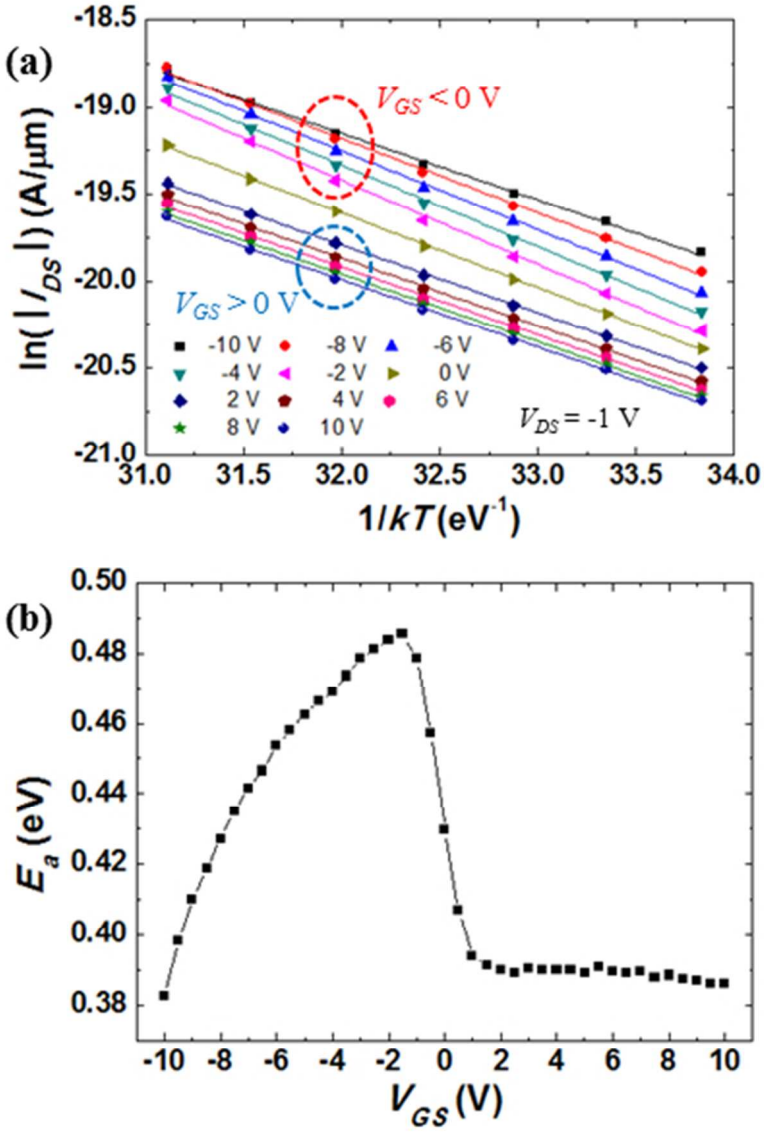

Figure 3

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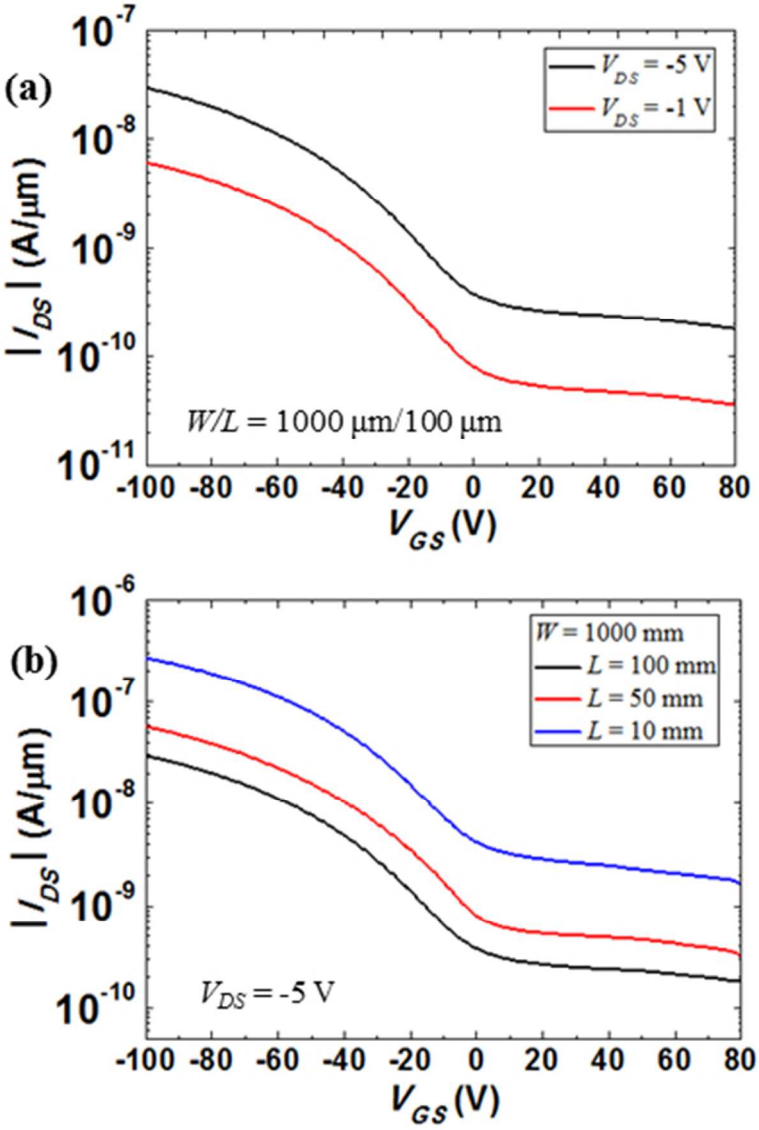

Figure 4

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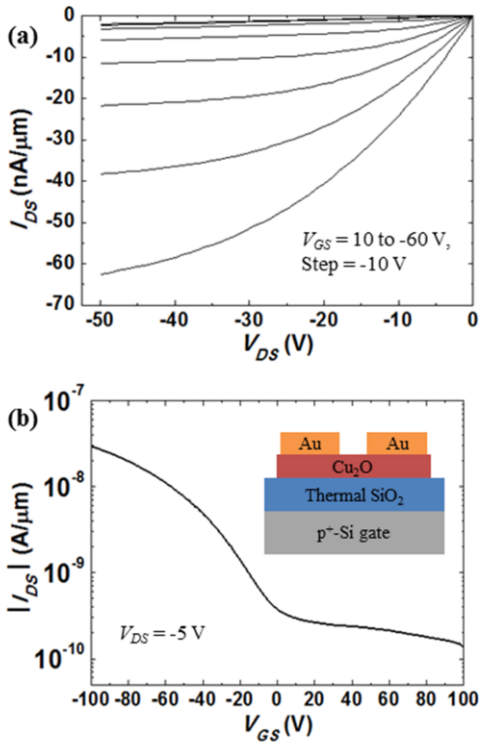

Fig. 1. (a) Output and (b) transfer characteristics of a typical fabricated Cu_2O TFT. The inset is a schematic structure of the Cu_2O TFT.

negative gate voltage (V_{GS}). However, Fig. 1 (b) shows a high off-state current and thus a low on/off current ratio (~2×10^2), which is consistent with previously-reported observations [7], [8], [10].

Figure 2 shows the C-V characteristic of the Cu_2O MOS capacitor. Contrary to n-type metal oxides such as IGZO showing only majority carrier (electron) accumulation [14], [15], interestingly, this shows that not only holes are accumulated at V_{GS} < 0 V (i.e. in the on-state region) but also electrons are accumulated at V_{GS} > 0 V (i.e. in the off-state region). Calculated results of formation energies for intrinsic defects in Cu_2O as a function of the Fermi energy (E_F) [6], [16] provide a possible interpretation of the electron accumulation.

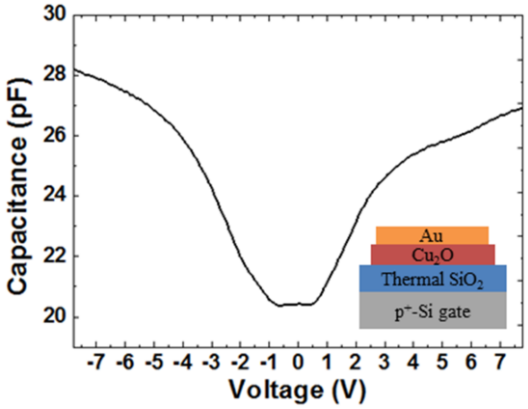

Fig. 2. The low frequency (500 kHz) C-V characteristic of a Cu_2O MOS capacitor. The inset is a schematic structure of the capacitor.

To be specific, since the main hole producer, copper vacancies (V_{Cu}), has the lowest formation energy with a small $\varepsilon(0/-)$ ionization level at E_V + 0.28 eV, Cu_2O has intrinsic p-type conductivity. However, other defects, such as oxygen vacancies (V_O) and copper interstitials (Cu_i), can act as potential donors for minority carriers (electrons) in Cu_2O. V_O do not have a charge transition level in the band gap, which means that they are only stable in the charge-neutral state and thus cannot act as donors [6], [16]. In contrast, Cu_i are amphoteric defects with both $\varepsilon(+/0)$ and $\varepsilon(0/-)$ charge transitions in the band gap; $\varepsilon(+/0)$ lies at ~1.3 eV above the VBM (i.e. Cu_i have a positive charge state Cu_i^+ when $E_F - E_V$ < 1.3 eV) [6], [16]. This means that they would act as donors for minority carriers in p-type Cu_2O, suggesting that the electron accumulation at V_{GS} > 0 V can be due to minority carriers created by Cu_i in Cu_2O.

In order to verify that electron flow is the source of the high off-state current, the activation energy (E_a) extracted from the temperature dependence of I_{DS} was investigated as a function of V_{GS}. I_{DS} is thermally activated and is described as

$$I_{DS} = I_{DS0}\exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

where I_{DS0}, k, and T are the prefactor, the Boltzmann constant and temperature [17], [18]. Here, E_a is the energy difference between E_F and either the edge of the valence band (i.e. $E_F - E_V$ for a p-type channel) or the conduction band (i.e. $E_C - E_F$ for an n-type channel). Equation (1) can be written as

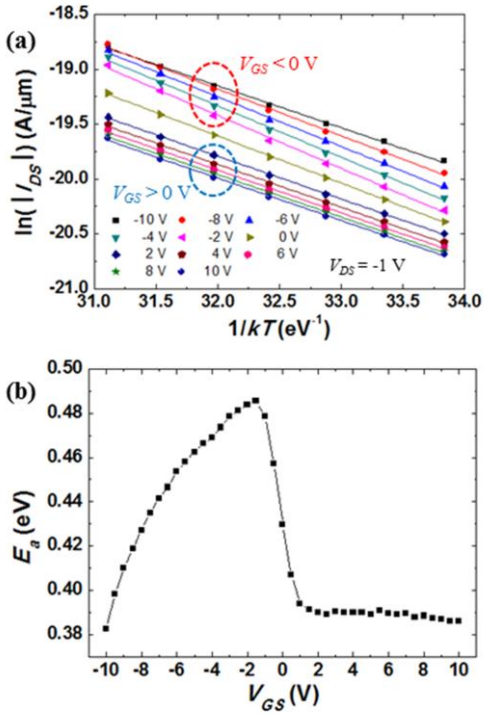

Fig. 3. (a) Temperature dependence of the drain current obtained at various V_{GS} and a fixed V_{DS} of -1 V; scatter dots are measured data and the line gradients are used for extracting the activation energy (E_a), and (b) extracted activation energy as a function of V_{GS}.

$\ln(|I_{DS}|) = (-E_a)(1/kT) + \ln(|I_{DS0}|)$, and as a result E_a can be extracted from the gradient of an $\ln(|I_{DS}|)$ versus $1/kT$ graph, as seen in Fig. 3 (a). The extracted E_a as a function of V_{GS} is shown in Fig. 3 (b). In contrast to the usual case where E_a increases in the off-state region (see the case of n-type IGZO TFTs [17]), Fig. 3 (b) shows an abrupt lowering of E_a in the off-state region. This can be understood to be due to E_F movement from near the VBM to near the conduction band minimum (CBM) based on the C-V characteristic (i.e. the channel inverts from p-type to n-type). The change in the temperature dependence of I_{DS} at V_{GS} > 0 V (i.e. an abrupt reduction in the slope, see Fig. 3 (a)) also suggests that the electron flow is the source of the high off-state current.

In addition, it is observed that E_F is not modulated by V_{GS} in the off-state region (see Fig. 3 (b)). This normally indicates pinning of the Fermi energy [19], which in this case is attributable to subgap states in the upper half of the band gap. Photoconductivity [20] and photoluminescence [21] results show that there is a subgap state at ~0.38 eV below the CBM in Cu_2O, and the authors attributed the origin of the subgap states to V_O. However, density-functional theory (DFT) analysis [16] strongly suggests that since the V_O level lies below the VBM, V_O cannot be the source of this subgap state. Although the origin of these subgap states is not certain, it is likely that it is the same states that are observed in photoconductivity and photoluminescence measurements which result in the E_F pinning observed in the TFTs in this work, and this results in the accumulation of electrons in the off-state and the high off-state current.

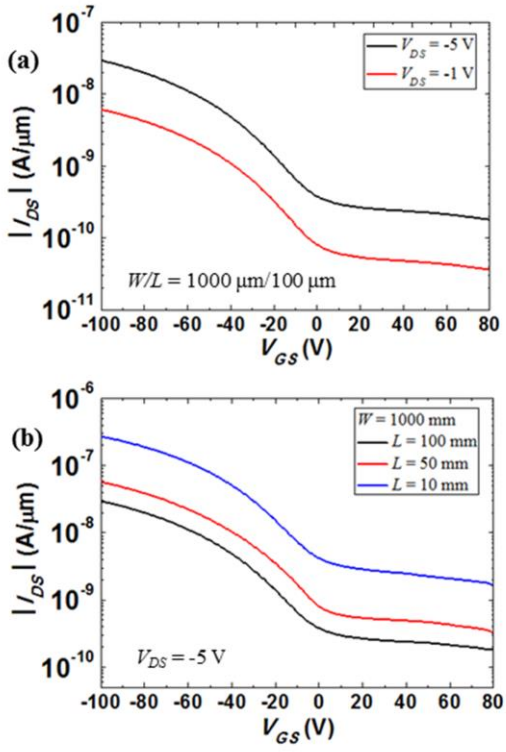

Fig. 4. Transfer characteristics as a function of (a) V_{DS} at W/L = 10, and (b) the channel width-to-length ratio (W/L) at V_{DS} = -5 V.

Figure 4 shows transfer characteristics as a function of V_{DS} and W/L. Contrary to n-type IGZO TFTs with complete channel depletion in the off-state showing no dependence of the off-state current on V_{DS} [22] and W/L [23], this shows that the off-state current increases with an increase in $|V_{DS}|$ (see Fig. 4 (a)) and a reduction in the channel length (see Fig. 4 (b)). The channel length dependence of the off-state current can be understood by a decrease in channel resistance attributable to the minority carrier (electron) accumulation with a reduction in the channel length. The dependence of the off-state current on V_{DS} and W/L provides further support for the finding that the high off-state current is due to minority carrier (electron) accumulation. This also results in significant degradation of the sub-threshold characteristic, and thus this leads to an excessively high sub-threshold slope (SS) of ~35 V/dec.

IV. Conclusion

The temperature dependence of the drain current as a function of gate voltage along with the C-V characteristics shows that minority carriers (electrons) cause the high off-state current in p-type Cu_2O TFTs, and not an inability to deplete the hole density in the channel. This electron accumulation in the off-state is considered to be due to minority carriers formed by Cu_i in Cu_2O. Based on reported results of photoconductivity and photoluminescence, pinning of the Fermi energy in the off-state could be due to the subgap states at ~0.38 eV below the CBM. Although the origin of these subgap states is not certain, reducing their density will be critical for improving the switching ratio in Cu_2O TFTs.

References

[1] E. Fortunato, P. Barquinha, and R. Martins, "Oxide semiconductor thin-film transistors: a review of recent advances," *Adv. Mater.*, vol. 24, no. 22, pp. 2945–2986, May, 2012. DOI: 10.1002/adma.201103228.

[2] E. Fortunato, V. Figueiredo, P. Barquinha, E. Elamurugu, R. Barros, G. Goncalves, S.-H. K. Park, C.-S. Hwang, and R. Martins, "Thin-film transistors based on p-type Cu_2O thin films produced at room temperature," *Appl. Phys. Lett.*, vol. 96, no. 19, p. 192102, May, 2010. DOI: 10.1063/1.3428434.

[3] H. Kawazoe, H. Yanagi, K. Ueda, and H. Hosono, "Transparent p-type conducting oxides: design and fabrication of p-n heterojunctions," *MRS Bull.*, vol. 25, no. 8, pp. 28–36, Aug. 2000. DOI: 10.1557/mrs2000.148.

[4] H. Yanagi, H. Kawazoe, A. Kudo, M. Yasukawa, and H. Hosono, "Chemical design and thin film preparation of p-type conductive transparent oxides," *J. Electroceram.*, vol. 4, no. 2-3, pp. 407–414, Jun. 2000. DOI: 10.1023/A:1009959920435.

[5] S. Han, K. M. Niang, G. Rughoobur, and A. J. Flewitt, "Effects of post-deposition vacuum annealing on film characteristics of p-type Cu_2O and its impact on thin film transistor characteristics," *Appl. Phys. Lett.*, vol. 109, no. 17, p. 173502, Oct. 2016. DOI: 10.1063/1.4965848.

[6] H. Raebiger, S. Lany, and A. Zunger, "Origins of the p-type nature and cation deficiency in Cu_2O and related materials," *Phys. Rev. B*, vol. 76, no. 4, p. 045209, Jul. 2007. DOI: 10.1103/PhysRevB.76.045209.

[7] K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, "Epitaxial growth of high mobility Cu_2O thin films and applications to p-channel thin film transistor," *Appl. Phys. Lett.*, vol. 93, no. 20, p. 202107, Nov. 2008. DOI: 10.1063/1.3026539.

[8] K. Matsuzaki, K. Nomura, H. Yanagi, T. Kamiya, M. Hirano, and H. Hosono, "Effects of post-annealing on (110) Cu_2O epitaxial films and origin of low mobility in Cu_2O thin-film transistor," *Phys. Status Solidi A*, vol. 206, no. 9, pp. 2192–2197, Aug. 2009. DOI: 10.1002/pssa.200881795.

[9] C.-Y. Jeong, J. Sohn, S.-H. Song, I.-T. Cho, J.-H. Lee, E.-S. Cho, and H.-I. Kwon, "Investigation of the charge transport mechanism and subgap

density of states in p-type Cu_2O thin-film transistors," *Appl. Phys. Lett.*, vol. 102, no. 8, p. 082103, Feb. 2013. DOI: 10.1063/1.4794061.

[10] S. Y. Kim, C. H. Ahn, J. H. Lee, Y. H. Kwon, S. Hwang, J. Y. Lee, and H. K. Cho, "p-channel oxide thin film transistors using solution-processed copper oxide," *ACS Appl. Mater. Interfaces*, vol. 5, no. 7, pp. 2417–2421, Mar. 2013. DOI: 10.1021/am302251s.

[11] P. Pattanasattayavong, S. Thomas, G. Adamopoulos, M. A. McLachlan, and T. D. Anthopoulos, "p-channel thin-film transistors based on spray-coated Cu_2O films," *Appl. Phys. Lett.*, vol. 102, no. 16, p. 163505, Apr. 2013. DOI: 10.1063/1.4803085.

[12] A. J. Flewitt, J. D. Dutson, P. Beecher, D. Paul, S. J. Wakeham, M. E. Vickers, C. Ducati, S. P. Speakman, W. I. Milne, and M. J. Thwaites, "Stability of thin film transistors incorporating a zinc oxide or indium zinc oxide channel deposited by a high rate sputtering process," *Semicond. Sci. Technol.*, vol. 24, no. 8, p. 085002, Jun. 2009. DOI: 10.1088/0268-1242/24/8/085002.

[13] S. Han and A. J. Flewitt, "Analysis of the conduction mechanism and copper vacancy density in p-type Cu_2O thin films," *Sci. Rep.*, vol. 7, 5766, Jul. 2017. DOI: 10.1038/s41598-017-05893-x.

[14] H. Choi, J. Lee, H. Bae, S.-J. Choi, D. H. Kim, and D. M. Kim, "Bias-dependent effective channel length for extraction of subgap DOS by capacitance–voltage characteristics in amorphous semiconductor TFTs," *IEEE Trans. Electron Devices*, vol. 62, no. 8, pp. 2689–2694, Jun. 2015. DOI: 10.1109/TED.2015.2443492.

[15] Y.-C. Tsao, T.-C. Chang, H.-M. Chen, B.-W. Chen, H.-C. Chiang, G.-F. Chen, Y.-C. Chien, Y.-H. Tai, Y.-J. Hung, S.-P. Huang, C.-Y. Yang, and W.-C. Chou, "Abnormal hump in capacitance–voltage measurements induced by ultraviolet light in a-IGZO thin-film transistors," *Appl. Phys. Lett.*, vol. 110, no. 2, p. 023501, Jan. 2017. DOI: 10.1063/1.4973856.

[16] D. O. Scanlon and G. W. Watson, "Undoped n-type Cu_2O: fact or fiction?," *J. Phys. Chem. Lett.*, vol. 1, no. 17, pp. 2582–2585, Aug. 2010. DOI: 10.1021/jz100962n.

[17] C. Chen, K. Abe, H. Kumomi, and J. Kanicki, "Density of states of a-InGaZnO from temperature-dependent field-effect studies," *IEEE Trans. Electron Devices*, vol. 56, no. 6, pp. 1177–1183, Jun. 2009. DOI: 10.1109/TED.2009.2019157.

[18] W. B. Jackson, J. M. Marshall, and M. D. Moyer, "Role of hydrogen in the formation of metastable defects in hydrogenated amorphous silicon," *Phys. Rev. B*, vol. 39, no. 2, pp. 1164–1179, Jan. 1989. DOI: 10.1103/PhysRevB.39.1164.

[19] K. Takechi, M. Nakata, T. Eguchi, H. Yamaguchi, and S. Kaneko, "Temperature-dependent transfer characteristics of amorphous $InGaZnO_4$ thin-film transistors," *Jpn. J. Appl. Phys.*, vol. 48, no. 1R, p. 011301, Jan. 2009. DOI: 10.1143/JJAP.48.011301.

[20] M. Zouaghi, B. Prevot, C. Carabatos, and M. Sieskind, "Near infrared optical and photoelectric properties of Cu_2O. III. Interpretation of experimental results," *Phys. Status Solidi A*, vol. 11, no. 2, pp. 449–460, Jun. 1972. DOI: 10.1002/pssa.2210110207.

[21] R. Garuthara and W. Siripala, "Photoluminescence characterization of polycrystalline n-type Cu_2O films," *J. Lumin.*, vol. 121, no. 1, pp. 173–178, Nov. 2006. DOI: 10.1016/j.jlumin.2005.11.010.

[22] W. Kang, C. Ahn, M. Yun, S. Cho, Y. Kim, D. Kim, B. Kim, H. Cho, and Y. Kim, "Expedient floating process for ultra-thin InGaZnO thin-film-transistors and their high bending performance," *RSC Adv.*, vol. 6, no. 68, pp. 63418–63424, Jul. 2016. DOI: 10.1039/C6RA06372A.

[23] W. Wang, L. Li, C. Lu, Y. Liu, H. Lv, G. Xu, Z. Ji, and M. Liu, "Analysis of the contact resistance in amorphous InGaZnO thin film transistors," *Appl. Phys. Lett.*, vol. 107, no. 6, p. 063504, Aug, 2015. DOI: 10.1063/1.4928626.

UNIVERSITY OF CAMBRIDGE
Department of Engineering

Professor Andrew Flewitt
Professor of Electronic Engineering

Editor,
IEEE Electron Device Letters

Monday, 28 August 2017

Dear Editor,

Re: Revision of Manuscript

We would like to thank you and the reviewers for the feedback on the recently-submitted article entitled *'The Origin of the High Off-State Current in p-Type Cu_2O Thin Film Transistors'* for publication in *Electron Device Letters.*

We have submitted a revised version of the article, on which I will comment on a point-by-point basis here.

Reviewer 1
Comment 1

Reviewer wrote: A minor shortcoming of the paper is the lack of device-to-device statistics. To fully support the affirmation, a range of devices with e.g. different *W/L* as well as identical geometry should be characterised, to show that J_{off} is consistent with the mechanism proposed.

Our response: A new figure (Fig. 4 (b)) showing transfer characteristics as a function of *W/L* has been added in the revised manuscript, which shows that the off-state current characteristic is consistent with the mechanism proposed. The corresponding paragraph has also been added in the revised manuscript.

Corresponding change in manuscript: Yes
Location of Change: Figure 4 (b) and the last paragraph have been added in Section III on page 3.

Reviewer 2
Comment 1

Reviewer wrote: When TFT typical I-V characteristics are shown at the beginning of the Section III for the off-region, a sub-threshold slope (SS) would be useful to quote at a selected V_{DS} for a better illustration of off-current behaviour of the transistor.

Our response: The SS characteristic has been added in the revised manuscript.

Corresponding change in manuscript: Yes
Location of Change: This has been added in the last sentence of Section III on page 3.

Reviewer 2
Comment 2

Reviewer wrote: One more transfer characteristic (I_{DS}-V_{GS}) at properly selected V_{DS}, say between -1.0 V to -4.0 V or so, should be added into Fig. 1(b) to give readers a better understanding of the device behaviour at a low drain bias. The SS can be quoted for this characteristic as well.

Our response: Instead of adding the transfer characteristic at V_{DS} = -1 V into Fig. 1 (b), a new figure (Fig. 4 (a)) showing transfer characteristics at V_{DS} = -1 V, -5 V has been added in the revised manuscript in order to show dependence of the off-state current on V_{DS} as well as *W/L*.

Corresponding change in manuscript: Yes
Location of Change: Figure 4 (a) has been added in Section III on page 3.

Reviewer 2
Comment 3

Reviewer wrote: (Optional) Abstract could contain one of the main results of the work, a location of the subgap states which is responsible for the large off-current.

Our response: This statement has been added in abstract.

Corresponding change in manuscript: Yes
Location of Change: Abstract

Reviewer 2
Comment 4

Reviewer wrote: (Optional) The expression 'This suggests that E_F becomes closer to...' does not seem to be describing well the undergoing physical process, should be reformulated??

Our response: The abrupt lowering of the activation energy (E_a) in the off-state region can be explained by the Fermi energy movement from near the VBM to near the CBM on the basis of the C-V characteristic showing electron accumulation in the off-state region (i.e. the channel inversion from p-type to n-type). For this reason, the authors think that the expression provides a reasonable interpretation of the abrupt E_a lowering. In order to describe it more clearly, the statement has been reformulated.

Corresponding change in manuscript: Yes
Location of Change: The first paragraph on page 3.

Having made these changes to the paper, I would be grateful if this could be considered again for publication.

Yours sincerely,

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