Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information (ESI)

Low-temperature, Inkjet Printed p-type Copper (I) Iodide Thin Film Transistors

Chang-Ho Choi,^a Jenna Y. Gorecki,^a Zhen Fang,^a Marshall Allen,^a Shujie Li, ^a Liang-Yu Lin,^b Chun-Cheng Cheng,^b Chih-Hung Chang^a*

^a Oregon Process Innovation Center/ Microproduct Breakthrough Institute and School of Chemical, Biological & Environmental Engineering, Oregon State University, Corvallis, Oregon 97331, United States

^b AU Optronics Corporation, No.1, Li-Shin Rd., Hsinchu Science Park, Hsinchu, Taiwan

*E-mail: <u>Changch@che.orst.edu</u>

Experimental

Materials

Copper(I) iodide (γ-CuI, anhydrous, 99.995%) were purchased from Sigma-Aldrich. A solvent of acetonitrile (HPLC>99.9%) was purchased from Fisher Scientific. SU-8 photoresist (SU-8, 2010) was purchased from Microchem.

Fabrication of printed CuI TFTs

SiO₂/Si substrates were used to fabricate printed CuI TFTs. The back side of the substrate was deposited with gold (Au) layer of 100 nm thickness. Oxide layer of 100nm thickness was thermally grown on the silicon substrate as a dielectric layer. All of the substrates were treated through oxygen plasma process to clean the substrate. 0.05 M CuI solution was dissolved in acetonitrile solvent, followed by ultrasonication for 30 min. The solution then was filtered with a syringe filter (Nonsterile, PTFE 25mm x 0.20um). The filtered precursor solution served as a printing ink without any additives. Piezoelectric inkjet printer (Dimatix DMP-2831, Fujifilm) was used to manufacture the CuI film. The dimension of the printed film was controlled by software installed in the printer. The deposition temperature was tuned from room temperature to 60 °C. As-printed film was placed on a hot plate set to 120 °C for 30 min. to evaporate the solvent. A gold layer of 50nm thickness then was deposited as source and drain by thermal evaporator using a shadow mask for patterning. The active channel layer was defined as 1000 µm and 200 µm for width and length, respectively. After depositing source and drain, the device was placed on a hot plate at 150°C for 30min in order to keep the device from the moisture. Then, SU-8 was applied on the printed CuI channel layer as a passivation layer in order to prevent moisture and impurities from affecting device performances.

Characterization

Optical, electrical, and morphological properties of CuI films were investigated. The crosssectional morphology of the CuI films was characterized by scanning electron microscopy (SEM, FEI Helios 650). Atomic force microscope (AFM, Veeco Nanoscope digital instruments) was employed to analyze the surface morphology and roughness of the films. The films were characterized by X-ray diffraction (XRD, Bruker D8 discover) to investigate the crystalline structure. The optical properties of the films were studied using UV-vis spectroscopy (Jasco, V-670 Spectrophotometer). Electrical properties of the film were analyzed by using Hall effect measurement (Ecopia, HMS-5000). For analysis of optical properties and electrical properties, CuI film was printed on bare soda lime glass substrate. Device performances of the printed CuI TFTs were measured using an Agilent Technologies E5270B Semiconductor Parameter Analyzer under ambient conditions.



Figure S1. Mobility values of (g) printed CuI TFTs at room temperature and (h) printed CuI TFTs at 60 °C as a function of gate voltage.





Figure S2. Characterization of CuI TFTs printed at 60 °C: (a) output characteristic curves, (b) hysteresis and gate leakage current measurement.



Figure S3. Characterization of printed CuI TFTs baked at 150 °C: (a) XRD pattern, (b) band gap measurement, and (c) AFM image.

| | Material | Process | Mobility (cm ² / Vs) | On/Off ratio | Reference |
|-------------------------------|-----------------------|-------------------------|------------------------------------|----------------------|-----------|
| Vacuum- based process | SnO _x | Rf magnetron sputtering | 1.1-1.2 | 10 ³ | [1] |
| | SnO | Sputtering | 3.24 | 10 ³ | [2] |
| | Cu ₂ O/SnO | Sputtering | 0.66 | 1.5×10 ² | [3] |
| | Cu ₂ O | Magnetron sputtering | 2.40 | 3.96×10 ⁴ | [4] |
| | CuO | Thermal oxidation | 1.9 | 10 ² | [5] |
| Solution- based process | Cu ₂ O | spin coating | 0.16 | 10 ² | [6] |
| | Cu ₂ O | Spray pyrolysis | 0.01 | 4×10 ³ | [7] |
| | Cu ₂ O | Spin coating | 0.29 | 1.6×10 ⁴ | [8] |
| | CuO | Spin coating | 0.01 | 10 ³ | [9] |
| | SnO | Spin coating | 0.13 | 10 ^{1.9} | [10] |
| | CuI | Inkjet printing | 1.86 | 10 ² | This work |
| | CuO | Spin coating | 0.8 | 10 ⁵ | [11] |
| | NiOx | Spin coating | 0.97 | 9.8×10^5 | [12] |
| | NiOx | Spin coating | 4.4 | 10^{5} | [13] |
| | CuO | Inkjet print | 0.22 | 10 ³ | [14] |
| | | | | | |

Table S1. Summary of reported p-type metal oxide TFTs

References

- [1] E. Fortunato, R. Barros, P. Barquinha, V. Figueiredo, S. H. K. Park, C. S. Hwang, R. Martins, *Appl. Phys. Lett.* 2010, 97, 052105.
- [2] C.-W. Zhong, H.-C. Lin, K.-C. Liu, T.-Y. Huang, Jpn. J. Appl. Phys. 2016, 55, 016501.
- [3] H. A. Al-Jawhari, J. A. Caraveo-Frescas, M. N. Hedhili, H. N. Alshareef, ACS Appl. Mater. Interfaces, 2013, 5, 9615–9619.
- [4] Z. Q. Yao, S. L. Liu, L. Zhang, B. He, A. Kumar, X. Jiang, W. J. Zhang, G. Shao, *Appl. Phys. Lett.* 2012, **101**, 042114.
- [5]. V. Figueiredo, J. V. Pinto, J. Deuermeier, R. Barros, E. Alves, R. Martins, E. Fortunato, J. Disp. Technol. 2013, 9, 735.
- [6] S. Y. Kim, C. H. Ahn, J. H. Lee, Y. H. Kwon, S. Hwang, J. Y. Lee and H. K. Cho, ACS. Appl. Mater. Inter., 2013, 5, 2417-2421.
- [7] P. Pattanasattayavong, S. Thomas, G. Adamopoulos, M. a. McLachlan, T. D. Anthopoulos, *Appl. Phys. Lett.* 2013, **102**, 163505.
- [8] J. M. Yu, G. X. Liu, A. Liu, Y. Meng, B. Shin and F. K. Shan, *J. Mater. Chem. C*, 2015, 3, 9509-9513.
- [9] J. Jang, S. Chung, H. Kang, V. Subramanian, *Thin Solid Films*, 2016, 600, 157.
- [10] K. Okamura, B. Nasr, R. A. Brand and H. Hahn, J. Mater. Chem., 2012, 22, 4607-4610.
- [11] A. Liu, G. X. Liu, H. H. Zhu, H. J. Song, B. Shin, E. Fortunato, R. Martins and F. K. Shan, *Adv. Funct. Mater.*, 2015, 25, 7180-7188.
- [12] T. D. Lin, X. L. Li and J. Jang, Appl. Phys. Lett., 2016, 108, 233503

- [13] A. Liu, G. X. Liu, H. H. Zhu, B. Shin, E. Fortunato, R. Martins and F. K. Shan, *Appl. Phys. Lett.*, 2016, **108**, 233053.
- [14] S. K. Garlapati, T. T. Baby, S. Dehm, M. Hammad, V. S. K. Chakravadhanula, R. Kruk,H. Hahn and S. Dasgupta, *Small*, 2015, 11, 3591-3596.