

Solution-Processing of Inorganic and Hybrid Materials for Flexible Electronics

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ABSTRACT

To improve the electrical properties in solution-processed high-performance, large-area flexible electronics, we employed hybrid structures of a multifunctional organic-semiconductor/amorphous oxide semiconductor, nanomaterials/amorphous oxide semiconductors, and chalcogenide-gel. With the novel hybrid structures and new processing strategy, we could demonstrate enhancement of mobility, electrical stability, and exceptional mechanical stability.

1 INTRODUCTION

The recent development of large area electronics have been focused on high electrical performance, novel mechanical functionality, high electrical stability, and exotic chemical stability under harsh condition. Especially the synergetic combinations of mechanical functionality and other functionalities opened new era of flexible electronics, such as flexible display, rollable display, and wearable electronics.

To achieve the unprecedented functionalities and its combination, numerous materials have been investigated with new material design and novel processing strategy. For example, organic semiconductors have been pursued with superior mechanical flexibility and facile material design. The nanomaterials have shown its promising optoelectronic properties and exotic electronic functionalities with its unique shape and size dependent nature. Amorphous oxide semiconductors, such as a-IGZO, have been successfully implemented for commercial high end display applications, such as organic light emitting diode display. Unfortunately, these efforts cannot fulfill the emerging demands on complicated material functionality with high electronic performances. In addition, high cost vacuum processing method hindered the new application area, such as disposable electronics, smart packaging, and ultra large area electronic devices.

Our group have worked on the development novel materials and low cost solution processing strategy.¹⁻⁴ Although the organic materials and inorganic materials have been investigated with diverse approaches, the combination of these materials as hybrid materials might result synergetic effects for unprecedented properties.¹⁻² Also the innovative processing strategy for metal

chalcogenide with low cost solution process could provide alternative method to deposit metal chalcogenide for large area display, photovoltaics, and sensors.³⁻⁴

2 RESULTS

To achieve the stabilization and control of the electrical properties in solution-processed amorphous-oxide semiconductors (AOSs) for the realization of cost-effective, high-performance, large-area electronics, we employ a multifunctional organic-semiconductor (OSC)/a solution-processed thin-film hybrid structure.¹ In particular, impurity diffusion, electrical instability, and the lack of a general substitutional doping strategy for the active layer hinder the industrial implementation of copper electrodes and the fine tuning of the electrical parameters of AOS-based thin-film transistors (TFTs). The multifunctional organic-semiconductor (OSC) interlayer acted as a solution-processed thin-film passivation layer and a charge-transfer dopant. As an electrically active impurity blocking layer, the OSC interlayer enhances the electrical stability of AOS TFTs by suppressing the adsorption of environmental gas species and copper-ion diffusion. Moreover, charge transfer between the organic interlayer and the AOS allows the fine tuning of the electrical properties and the passivation of the electrical defects in the AOS TFTs. The development of a multifunctional solution-processed organic interlayer enables the production of low-cost, high-performance oxide semiconductor-based circuits.

Furthermore, the proper design of organic/inorganic hybrid structure resulted exceptional electrical stability under harsh high energetic proton irradiation, which makes our device promising for aerospace application.² The 5 MeV high-energy proton irradiation on solution-processed metal-oxide thin-film transistors (TFTs) have been performed for various devices, such as ZnO, IGZO, ZTO and hybrid devices. The electrical characteristics of the devices are measured before and after proton irradiation with radiation doses of 10^{13} , 10^{14} , and 10^{15} cm⁻². TFTs based on zinc oxide (ZnO) and amorphous indium gallium zinc oxide (a-IGZO) exhibit a significant negative shift in their threshold voltage values ($\Delta V_{th} \leq -30$ V) or transitioned to the conductor state as the proton radiation dose increased. For a-ZnO and IGZO,

this change in the electrical characteristics originates from the formation of proton-irradiation-induced oxygen vacancies in the metal-oxide semiconductor layer. On the other hand, amorphous zinc tin oxide devices with an optimized composition exhibit relatively stable electrical characteristics when subjected to proton irradiation. Furthermore, the back-channel passivation of oxide-semiconductor TFTs with an n-type organic semiconductor layer significantly improves the device stability under proton irradiation. This study demonstrates that solution-processed metal-oxide semiconductors have significant potential as rad-hard large area electronic devices for nuclear and aerospace applications.

Unlike metal oxide, the solution processing of metal chalcogenide have relied on limited materials scope. One possible method is using soluble nanocrystals with long organic ligands. However the facile removal of organic ligand to improve the carrier transport have been significant issues. The recent developments of short inorganic ligands enabled high performance thin-film transistor with nanocrystals.⁵⁻⁶ Moreover the facile passivation on defect states on nanocrystal surfaces have been demonstrated with deposition of indium layer.⁶ However, these methods suffered from toxic solvent usage, high instability against air exposure, or low electrical performance. Without using toxic solvent, our group have demonstrated high performance nanocrystal based thin-film transistor with high electron motility of 44.2 cm²/Vs. We employed solid state synthesis for metal chalcogenide capping ligand and soluble indium nanocrystal for all solution processed stable nanocrystal based thin-film transistor fabrication. Moreover, the molecular precursor design with chalco-gel strategy enabled us to deposit broad range of metal chalcogenide without limitation of materials choice.⁴ We have deposited PbQ, CdQ, ZnQ, In₂Q₃, Sb₂Q₃ and its alloy thin films. Especially, the CdSe based thin-film transistor showed extremely high electronic motility over 300 cm²/Vs. Furthermore, the scalability and large area uniformity of our methods have been confirmed with thin-film transistor devices and seven-stage ring oscillator on 4-inch wafer and 2.5-inch borosilicate glass substrates.

3 CONCLUSIONS

The flexible electronic applications still needs further development of materials and processing methods. Our works on organic-inorganic hybrid materials, nano materials, and chalco-gel will contribute facile realization of high performance large area electronic applications with low cost and high throughput solution process.

REFERENCES

- [1] G. Kwon, K. Kim, B. D. Choi, J. Roh, C. Lee, Y.-Y. Noh, S.Y. Seo, M.-G. Kim and C. Kim "Multifunctional Organic - Semiconductor Interfacial Layers for

Solution - Processed Oxide - Semiconductor Thin - Film Transistor", *Adv. Mater.*, Vol. 29, No. 21, pp. 1607055 (2017)

- [2] B. Park, D. Ho, G. Kwon, D. Kim, S. Y. Seo, C. Kim and M. - G. Kim "Solution - Processed Rad - Hard Amorphous Metal - Oxide Thin - Film Transistors" *Adv. Funct. Mater.*, Vol. 28, No. 47, pp. 1802717 (2018)
- [3] S. M. Jung, H. L. Kang, J. K. Won, J. Kim, C. Hwang, K. Ahn, I. chung, B.-K. Ju, M.-G. Kim and S. K. Park "High-Performance Quantum Dot Thin-Film Transistors with Environmentally Benign Surface Functionalization and Robust Defect Passivation" *ACS Appl. Mater. Interfaces*, Vol 10, No. 4, pp. 3739-3749 (2018)
- [4] S. Kwon, W. J. Won, J.-W. Jo, J. Kim, H.-J. Kim, H.-I. Kwon, J. Kim, S. Ahn, Y.-H. Kim, M.-J. Lee, H.-I. Lee, T. J. Marks, M.-G. Kim, and S. K. Park "High-performance and scalable metal-chalcogenide semiconductors and devices via chalco-gel routes" *Sci. Adv.*, Vol. 4, No. 4, pp. eaap9104 (2018)
- [5] M. V. Kovalenko, M. Scheele, D. V. Talapin. "Colloidal Nanocrystals with Molecular Metal Chalcogenide Surface Ligands." *Science* Vol. 324, No. 5933, pp.1417-1420 (2009).
- [6] J.-H. Choi, S. J. Oh, Y. Lai, D. K. Kim, T. Zhao, A. T. Fafarman, B. T. Diroll, C. B. Murray, C. R. Kagan "In Situ Repair of High-Performance, Flexible Nanocrystal Electronics for Large-Area Fabrication and Operation in Air", *ACS Nano* Vol. 7, No. 9, pp. 8275-8283 (2013)