## **Electronic Properties and Device Fabrication of Soluble Organic-Inorganic Copper Halide Based Perovskites**

°Giancarlo S. Lorena<sup>1</sup>, Tsuyoshi Osaki<sup>2</sup>, Hiroyuki Hasegawa<sup>2,3</sup>, Yukihiro Tahashi<sup>1,2,3</sup>, Jun Harada<sup>1,2,3</sup>, Tamotsu Inabe<sup>1,2,3</sup>

<sup>1</sup> Graduate School of Chemical Sciences and Engineering, Hokkaido Univ., <sup>2</sup> Faculty of Science, Hokkaido Univ., <sup>3</sup> CREST, Japan Science and Technology Agency

E-mail: g.lorena@cse.hokudai.ac.jp; inabe@sci.hokudai.ac.jp

Recently, organic-inorganic perovskite based on lead halide have also been incorporated as sensitizers and electrode for solar cell applications<sup>1-3</sup>. The electronic structure of perovskite compounds can be controlled by substitution of its constituent elements. These can be seen in dielectrics, semiconductors, ferroelectrics, piezoelectrics, superconductors, etc. Derived from these compounds, are soluble organic-inorganic hybrid perovskites which combine the robustness of inorganic components and the flexibility of organic compounds. These hybrid compounds have been shown to be electronically tunable and solution processable<sup>4</sup>.

NH<sub>3</sub> COOCH2CH3 Fig 1. Chemical Structure of EAC

16p-C5-12

In this study, we focused on organic-inorganic copper-halide based perovskite compounds with the formula  $R_2CuX_4$  (R= organic cation and X= Cl, Br), these compounds are far less toxic compared to lead based perovskites. For (EAC)<sub>2</sub>CuBr<sub>4</sub> (EAC ethyl-(4-ammoniummethyl)cyclohexanecarboxylate, Fig.1) the optical band is about 1.1 eV (Fig.2) and the room temperature resistivity is  $7.8 \times 10^{10}$   $\Omega$  cm. In addition, these compounds are easily synthesized using a variety of solvents like water, ethanol and methanol and they can form good thin films simply by spin coating technique. These properties, opens up possibilities for easy device fabrication.



Fig. 2. Optical band gap of (EAC)<sub>2</sub>CuBr<sub>4</sub>

We first investigated the effect of carrier injection by two chemical doping methods. One is carrier doping by substitution of Cu<sup>II</sup> with Cu<sup>I</sup> in (EAC)<sub>2</sub>CuBr<sub>4</sub>, and the other is contact-type carrier doping by placing an electron donating material in contact with the sample crystal. In the case of the doping by substitution of Cu<sup>II</sup> with Cu<sup>I</sup>, the *I-V* characteristics indicate one order of magnitude higher conductivity than undoped (non-substituted) crystals (Fig. 3). In the other case, contact doping with tetramethyl-p-phenylenediamine (TMPD, Fig.4) on the surface of R<sub>2</sub>CuX<sub>4</sub> crystals exhibits one order of magnitude higher conductivity than



Fig. 4. Chemical structure of TMPD as-grown crystals. Surprisingly, its conductivity returned to its initial value when the dopant was removed. This switching effect was observed several times. From these results, it was found out that the chemical doping into these compounds is effective for carrier injection.

Doped (EAC)<sub>2</sub>CuBr 4.4x10<sup>9</sup> Ω·cn rent/nA Curr grown(EAC)2CuBr4  $\rho = 7.8 \times 10^{10} \,\Omega \cdot \mathrm{cm}$ -100 100 Voltage/V

Fig. 3. I-V characteristics of (EAC)<sub>2</sub>CuBr<sub>4</sub>

Furthermore, due to the solution processability of these hybrids, device fabrication by material printer (ink-jet patterning system) was performed. Electrodes were printed onto the silicon substrate using nanoinks of electrode materials. Then we also printed the solution of these copper-halide based perovskites after the bake process of electrodes. We attempted to fabricate field-effect tran-

sistors and solar cells using this method.

Further details on the electronic properties and device fabrication of these class of materials will be discussed.

## References

[1] M. Lee, T. Miyasaka, et. al. Science 338 (2012) 643. [2] A. Kojima, T. Miyasaka, et. al. J. Am. Chem. Soc. 131 (2009) 6050.

[3] I. Chung, et. al., Nature 485 (2012) 486. [4] Y.Takahashi, T. Inabe, et. al. Chem. Mater. 19 (2007) 6312.