

Copper Gallium Selenide based Photocathode for Sunlight driven Water Splitting  
 Tsutomu Minegishi, Salim Umar, Li Zhang, Hiromu Kumagai, Jun Kubota and Kazunari Domen\*  
 Department of Chemical System Engineering,  
 The University of Tokyo  
 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan

Fossil resources such as petroleum, coal, and natural gas are essential fuels supporting the human energy society and they are also utilized as converted to indispensable bulk chemicals such as ammonia for fertilizers of food-production. However, they are reasonably predicted to be exhausted in the future and replacement of fossil fuels by renewable energy resources is unavoidable. Hydrogen is regarded as an energy carrier in the next generation if it is produced by renewable energy sources. Photoelectrochemical (PEC) water splitting is one possible means of generating hydrogen in an environmentally friendly manner, because it requires only semiconductor electrodes, water, and sunlight. To utilize solar energy efficiently, a photoelectrode should meet at least three requirements: an appropriate bandgap for sunlight absorption, suitable band positions for water reduction/oxidation, and stability under the required reaction conditions. Many semiconductor materials and a variety of configurations have been surveyed<sup>1</sup>, but satisfying performance has not yet been obtained in a practical manner.

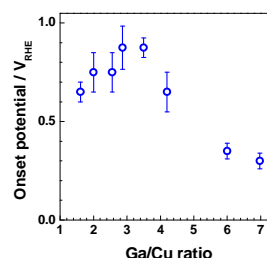
Copper chalcopyrite materials such as CuGaS<sub>2</sub> (1), CuInSe<sub>2</sub> (2), and Cu<sub>2</sub>ZnSnS<sub>4</sub> (CZTS) (3,4) attract considerable attentions as a photo-voltaic (PV) materials because of the good photo absorption, p-type conductivity and good performance in polycrystalline state and these merits are intersectional between PV and PEC.

We have studied copper gallium selenide (CGSe) as photocathodes through 2 approaches.(5,6) One is composition control to improve properties of these materials. Formation of ordered vacancy chalcopyrite (OVC) phase leads deepening of the ionization potential which results in higher flat band potential in photoelectrochemistry.(7) The other approach is the introduction of multi-layered structures to the electrode. Surface modifications using n-type semiconducting materials like CdS leads formation of p-n-liquid junction. The p-n junction formations with proper thickness of n-type layers thicken depletion layers without formation of undesired barriers.(8) In the present study, effects of composition and introduction of CdS top layer on the PEC properties of CGSe were investigated.

CGSe thin films were prepared on Mo coated glass plates by a vacuum co-evaporation method. Substrates were heated during film deposition and Cu (5N), Ga(6N) and Se(6N) were supplied onto the substrate surface by thermal evaporation. The film composition was determined by the controlled deposition ratio of Cu ( $J_{Cu}$ ), Ga ( $J_{Ga}$ ) and Se ( $J_{Se}$ ). Some CGSe samples were prepared under hydrogen partial pressure of  $\sim 10^{-3}$  Pa. To promote the hydrogen evolution reaction, Pt was deposited on the electrodes by photodeposition method. CdS layers were deposited by chemical bath deposition (CBD) method to thicken the depletion layer formed at the solid/liquid interface. Photoelectrochemical properties were characterized using 3-electrode system and/or 2-electrode system. Ag/AgCl and Pt wire were used as reference and counter for 3-electrodesystem. Structural properties were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron

microscopy (TEM).

SEM observation revealed that CGSe with Ga/Cu  $\sim 1$  showed large polygonal grains while the Ga rich samples showed flake shaped grains. In addition, a crystal structure of samples with Ga/Cu  $\sim 1$  was assigned to be chalcopyrite structure while a crystal structure of samples with Ga/Cu  $> 1.6$  was assigned to be defect compound phase by XRD measurement. Judging from these facts, the variations of surface morphology is caused by the phase transition from chalcopyrite phase to defect compound phase. The bare and Pt deposited CGSe films showed clear cathodic photo-response. An onset potential of Pt deposited CGSe are shown in Figure 1. An onset potential was maximum at Ga/Cu  $\sim 3$ . Bandgap broadening and VBM deepening with increasing Ga/Cu ratio were observed by photo reflection measurement and PESA. However, anodic photo-response around an onset potential was increased with Ga/Cu ratio. This result indicates the change of p-type CGSe to n-type. Consequentially, the onset potential was maximum around Ga/Cu  $\sim 3$ . Introduction of hydrogen during sample deposition resulted in larger grain size and cathodic photocurrent for CGSe with Ga/Cu of  $\sim 3$ . CBD of CdS top layer showed increase of onset potential and cathodic photocurrent for CGSe with Ga/Cu of  $\sim 1$  (9). Effects of the composition and introduction of multilayer structure were investigated. The composition has a great influence on the potential of band maximum with retaining p-type conductivity. The introduction of CdS top layers on the electrode surface enhanced photocurrent.



**Figure 1.** Onset potentials of photo-current from CGSe with various Ga/Cu composition ratios.

#### References

- (1) Shay, L.; Tell, B.; Kasper, H. M.; *Appl. Phys. Lett.* **1971**, 19, 366.
- (2) Conteras, M. A.; Ramanathan, K.; AbuShama, J.; Hasoon, F.; Young, I. L.; Egaas, B.; Noufi, R.; *Prog. Photovolt: Res. Appl.* **2005**, 13, 209.
- (3) Ito, K.; Nakazawa, T.; *Jpn. J. Appl. Phys.* **1988**, 27, 2094.
- (4) Katagiri, H.; Jimbo, K.; Maw, W. S.; Oishi, K.; Yamazaki, M.; Araki, H.; Takeuchi, A.; *Thin Solid Films* **2009**, 517, 2455.
- (5) Yokoyama, D.; Minegishi, T.; Maeda, K.; Katayama, M.; Kubota, J.; Yamada, A.; Konagai, M.; Domen, K.; *Electrochem Comm.* **2010**, 12, 851.
- (6) Yokoyama, D.; Minegishi, T.; Jimbo, K.; Hisatomi, T.; Ma, G.; Katayama, M.; Kubota, J.; Katagiri, H.; Domen, K.; *Appl. Phys. Express.* **2010**, 3, 101202.
- (7) Kim, J.; Minegishi, T.; Kubota, J.; Domen, K.; *Jpn. J. Appl. Phys.*, **2012**, 51, 015802
- (8) Kim, J.; Minegishi, T.; Kubota, J.; Domen, K.; *Energy Environ. Sci.*, **2012**, 5, 6368.
- (9) Moriya, M.; Minegishi, T.; Kumagai, H.; Katayama, M.; Kubota, J.; Domen, K.; *J. Am. Chem. Soc.*, **2013**, 135, 3733.