論 文 の 内 容 の 要 旨

論文題目　　Study on Copper Gallium Selenide Thin Film for the Photocathode of Water Splitting
（光電気化学的水分解用銅ガリウムセレナイド薄膜光カソードに関する研究）

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Chapter 1. General Introduction

Solar light driven direct hydrogen generation through photoelectrochemical (PEC) water splitting is a potential technique to obtain a renewable, sustainable energy source with high efficiency. Many attempts have been made to achieve efficient energy conversion from solar energy to hydrogen energy since the first report of TiO_2-based photoelectrolysis by Fujishima and Honda. However, the most significant obstacle is the lack of proper semiconductor materials that meet the demands for efficient and stable water splitting: a band gap of 1.6 to 1.9 eV with covering the redox potentials of the water, and chemical stability. The p-type Cu chalcopyrite semiconductor thin films with high efficiency as photovoltaic material have been developed and, recently, tried to apply to PEC water splitting. However, its performance in aqueous solution is not satisfactory for practical solar energy conversion to hydrogen due to insufficient energetic properties for water splitting, large overpotentials and so on. It is therefore a key issue to understand the dependence of PEC properties on band structure and film quality of Cu chalcopyrite materials. The object of this thesis is to clarify (i) the potential of ordered defect compound (ODC) of Cu chalcopyrite material with wide band gap for PEC photcathode, (ii) the relationship of PEC property and film quality, (iii) the relationship of cocatalyst loading amount and the possibility of the embodiment of highly efficient PEC cell using improved Cu chalcopyrite semiconductor thin film.

Chapter 2. Review of Experimental Methods

CGSe thin films were deposited on Mo-coated soda lime glass (SLG) substrates using a co-evaporation method. Heated samples and evaporation sources of high-purity elemental Cu (5N), Ga (6N), and Se (6N) equipped with shutters were placed in a vacuum chamber with a base pressure of around 1×10^{-6} Pa. The sample temperature was kept at 550 °C during film deposition. The beam fluxes of Cu, Ga, and Se were controlled by the temperature of their crucibles, and were kept constant throughout the deposition process. To reveal the effect of composition on band structure of CGSe film, the CGSe thin films with controlled Ga/Cu composition ratio were prepared by the ratio of evaporation fluxes. To declare the effect of Se vapor pressure on properties of $CuGa_3Se_5$, samples were prepared with various vapor flux ratio (J_{se}/J_{Cu+Ga}). In hydrogen irradiation experiments, pure H_2 gas (5N) was introduced into the vacuum chamber through a variable leak valve (VLV) during the evaporation of Cu, Ga, and Se. The hydrogen partial pressure was kept constant, between 0 and 5×10^{-3} Pa over the course of each deposition, except during sample cooling. In order to promote hydrogen generation, Pt particles were photoelectrochemically deposited on the surface of the CGSe film electrodes before measurements. This Pt photodeposition and the electrochemical characterization of Pt/CGSe electrode were executed in a three-electrode cell. In addition, ZnS layers were formed on the surface of CGSe thin films by CBD. To estimate the solar to hydrogen conversion efficiency (STH) of PEC cell using the modified CGSe film, two-electrode cell consisting of Pt/CGSe photocathode and RuO_2 anode was set up. 0.5 M Na_2SO_4 aqueous solution with pH 12 and solar simulator (AM 1.5G) were electrolyte and light source, respectively. The gas products analysis was also performed by using a gas chromatography.

Chapter 3. Effects of Compositions on Physical and Photoelectrochemical Properties of Copper Gallium Selenide Thin Film as a Photocathode for Water Splitting

The prepared CGSe film had a dense, rough surface consisting of flake-shaped grains 200~300 nm wide and 20~50 nm thick. XRD pattern of prepared CGSe film with a Ga/Cu ratio of 3.0 was analogous to that of $CuGaSe_2$ with chalcopyrite structure, indicating that prepared CGSe film had the structure of the $CuGaSe_2$-related defect compounds. The band gap values and VBM potentials of CGSe films were estimated using UV-vis. DRS measurements and photoelectron spectroscopy in air, respectively. With increasing Ga/Cu ratio, the band gap values increased up to 1.85 eV, and then saturated at a Ga/Cu ratio of 4. On the other hand, the potential of the VBM increased with increasing Ga/Cu ratio, up to 1.0 V_{NHE}. From the fact that valence band of $CuGaSe_2$ is constructed using the hybridized orbital of Cu *d* and Se *p*, the deepening of VBM of Cu-deficient compounds with the introduction of defect pairs could be understood.

Based on the current-potential curves for Pt/CGSe electrodes, PEC properties such as the photocurrent density at 0 V_{RHE} and the onset potential are profiled in Figure 1 as a function of the Ga/Cu ratio. Both values increased with increasing Ga/Cu ratio. However, a Ga/Cu ratio of >3.5 resulted in an abrupt decline of both. It is thought that the initial improvement of the photocurrent and onset potential was caused by deepen VBM, while the latter spoilage was likely due to the formation of n-type domains by anion defects such as Se vacancy. From these results, optimized Ga/Cu ratio was found to be in the range of 3 to 3.5. Pt deposited $CuGa_{3.0}Se_{5.2}$ film showed the photocurrent density of 4.95 mA/cm^2 under AM 1.5 G irradiation and the incident photon to current efficiency

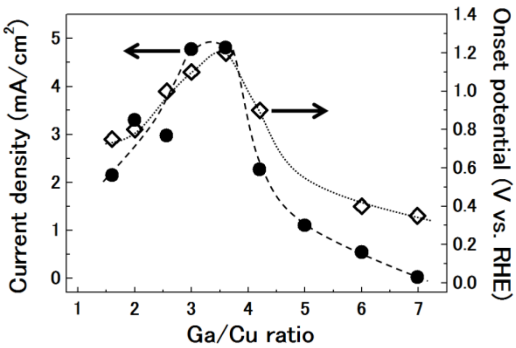

Figure 1. Dependence of photocurrent densities at 0 V_{RHE} (●) and onset potentials (◊) of Pt/CGSe electrode on composition.

(IPCE) of about 27%. This Pt/CGSe electrode produced a high onset potential of 1.1 V_{RHE} and a very high STH value of 0.35% comparable to the Pt/CIGS and Pt/CZTS. Therefore, CGSe is a promising candidate photocathode material for water splitting.

Chapter 4. Ehanced Photoelectrochemical Properties of $CuGa_3Se_5$ Films by Vapor Flux Control and Hydrogen Introduction during Deposition

The effect of the vapor flux on the structural properties of CGSe films was identified using XRD analyzing. The full width at half maximum (FWHM) values of the (112) diffraction peaks from samples deposited with J_{Se}/J_{Cu+Ga} of 1.79, 3.57, and 7.14 were 0.45, 0.76, and 1.09 degrees, respectively. This indicates that the increase in crystallite size of the CGSe films was induced by the decrease in Se flux during deposition. Showing the dependence of the surface composition ratio between Se and metals on the flux ratio, the composition analysis by EDX measurements revealed that the estimated composition ratios were constant till J_{Se}/J_{Cu+Ga} ratios of 5 to 1.27, and then increased with continuing increases in J_{Se}/J_{Cu+Ga}. This variation was likely due to the incorporation of excess Se into the film. For comparatively low Se fluxes, the composition ratio remained 1.27 because the supplied Se atoms were consumed in the growth of the CGSe crystal with Cu and Ga adatoms and a re-vaporization of excess Se. However, at higher Se fluxes, excess Se probably accumulates on the surface during deposition, leading to the formation of grain boundaries. The broadening of the FWHM in the XRD patterns with increasing J_{Se}/J_{Cu+Ga} can also be attributed to the diminishing grain size in the bulk CGSe due to excess Se and the shortening of the diffusion length of Cu and Ga adatoms. In addition, all of the XRD peaks of CGSe films grown at high J_{Se}/J_{Cu+Ga} were well matched to those of films grown at low J_{Se}/J_{Cu+Ga} without certain peaks attributed to excess Se.

On the other hand, I investigated the effect of hydrogen partial pressure on structural and photoelectrochemical properties of CGSe film. From a comparison of FWHM values in three dominant peaks of CGSe films grown under different hydrogen pressures, it was verified that only the FWHM of the (112) diffraction peaks varied considerably between samples prepared under different hydrogen partial pressures. FWHM values were 0.39, 0.47, 0.24 and 0.22 degree at hydrogen pressure of 0, 1×10^{-4}, 1×10^{-3} and 5×10^{-3} Pa, respectively. This implies that the hydrogen atmosphere causes an elongation of the migration length of atoms, enhancing crystal growth along a specific direction reflecting the feature of the material, i. e. vacancies are ordered along the <112> direction and the material tends to form platelets consisting of (112) crystal planes. The relationship between the FWHM of the (112) diffraction peaks that reflect the grain size of the CGSe

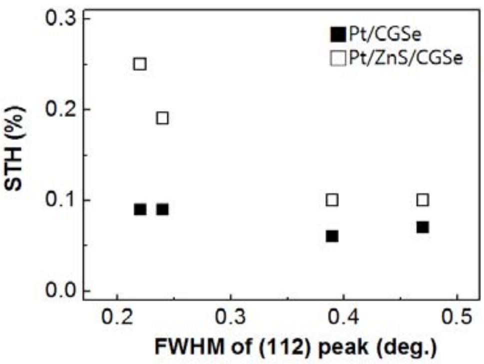

Figure 2. Variation in the values of STH with FWHM of the (112) peak in Pt/CGSe and Pt/ZnS/CGSe.

films and the STH values of Pt/CGSe and Pt/ZnS/CGSe photoelectrodes is profiled in Figure 2. With decreasing FWHM values (i.e., increasing grain size of CGSe) the increasing degree of STH values of photoelectrodes after ZnS deposition increased. Therefore, CGSe films with a large grain size are more suitable to form effective p-n junctions, which is consistent with the suggestion above that improved film structure prevents the n-type characteristic of CGSe by Zn ion diffusion through the grain boundaries. Therefore, hydrogen introduction during CGSe film growth improves the crystal quality, resulting in ZnS/CGSe photoelectrodes with a higher water splitting efficiency.

Chapter 5. Highly Efficient Photoelectrochemical Cell using Platinum Modified $CuGa_3Se_5$ Photocathode in Alkaline Solution

The energy conversion efficiency of ca. 1.05 % using Pt modified CGSe film as the PEC photoelectrode was achieved in alkaline solution. The Pt loading amount on CGSe film could be handled by the applied potential during the photoelectrochemical deposition, resulting in the large variance of IPCE and photocurrent in two and three electrodes cell test. Especially, Pt deposited CGSe at -0.65 $V_{Ag/AgCl}$ showed the highest Pt coverage and the largest photoelectrochemical properties. From the analysis of gas generated from Pt/CGSe and RuO_2 electrodes under light irradiation, it can be found that CGSe film is promising photocathode material for PEC water splitting with high faradaic efficiency.

Chapter 6. Summary

Polycrystalline CGSe thin films as $CuGaSe_2$-related Cu-deficient material were prepared by vacuum co-evaporation. The composition was adjusted in order to prepare CGSe film with an optimal band gap and VBM position for PEC water splitting. The effect of the Ga/Cu ratio on the PEC properties of CGSe was also studied. With increasing Ga/Cu ratio, the band gap of CGSe became larger, and the VBM position became deeper against the vacuum level. However, an analysis of the photocurrent and onset potential indicated that the Ga/Cu ratio should be less than 3.5 for optimal performance. Moreover, the influence of film deposition conditions during vacuum co-evaporation, including the flux ratio and the partial pressure of hydrogen, on the structural and PEC properties of CGSe films was examined. The flux ratio between Se and the other metals strongly affected both surface morphology and crystallite size. After ZnS modification, CGSe films grown at flux ratios (J_{Se}/J_{Cu+Ga}) of 3 to 5 had the highest energy conversion efficiency under AM1.5G irradiation. In addition, introducing hydrogen during the growth of CGSe films induced the selective growth of the (112) plane and an increase in grain size. ZnS-modified photocathodes using CGSe with an increased grain size due to hydrogen introduction had high solar energy conversion efficiencies because of their improved structural properties. Finally, I embodied the PEC cell using Pt modified CGSe film grown under hydrogen partial pressure and RuO_2 anode. With faradaic efficiency of almost 100%, a stoichiometric proportion of 2:1 between gas evolution rate of H_2 and O_2, and high STH of over 1.0% was observed.