別紙５－１（論文博士（英文））

Date of Submission (month day, year): July 9, 2018

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Abstract (Doctor)

Title of Thesis	Study on Fabrication and Characterization of Chalcogenide-based Thin Film Photovoltaic Devices of Environmental Harmony Type

Approx. 800 words

Recently, the many researches on renewable energy are carrying out to solve the environmental problems such as the depletion of fossil fuels and the global warming. Especially, the technologies of energy conversion using solar energy are spreading widely. Solar cells are electronic devices which converts solar energy directly into electrical energy through the photovoltaic effect. Now, many research organizations are researching the Cu_2ZnSnS_4-based solar cells as the chalcogenide-based thin film solar cells of the environmental harmony type which are composed of earth-abundant materials with no rare elements, low-cost and nontoxic. However, the safe fabrication methods which obtain the high conversion efficiency of the practical use level have not been established. Therefore, it is very important to investigate the characteristics of these solar cells fabricated by several methods with a safe process. This study has been performed from the above standpoint.

This thesis presents the investigation of the characteristics of the $Cu_2ZnSnSe_4$ and Cu_2SnS_3 thin films and solar cells fabricated by our proposed method such as vacuum evaporation, sulfurization and annealing methods.

First, the $Cu_2ZnSnSe_4$ thin films and solar cells were fabricated by the new vacuum evaporation method which used only the deposition stage using the $Cu_2ZnSnSe_4$ compound as the starting evaporation materials, and its characteristics were investigated. Furthermore, influences by annealing of the characteristics of these thin films and solar cells were investigated. The fabrication method of thin film solar cell using $Cu_2ZnSnSe_4$ compound is unprecedented, and our proposed method in this chapter is the first time. The film compositions, the film structures, the film morphologies, cell performances of these thin films and solar cells were characterized by electron probe microanalysis, X-ray diffraction, Raman spectroscopy, scanning electron microscopy, quantum efficiencies, and Current-voltage characteristics measurements, and these properties were discussed. The solar cells fabricated by this process had quantum efficiency in the wavelength range between 350 nm and 1400 nm. Therefore, the proposed method can be effectively used to produce thin films characterized by wide quantum efficiency ranges.

Next, the Cu_2SnS_3 thin films and solar cells were fabricated by sulfurization process from the stacked Cu/Sn precursors deposited by sequential evaporation of Sn and Cu elements. The

Cu/Sn molar ratio of the evaporation materials was changed, and the optimum value of the Cu/Sn molar ratio was investigated. The film composition, the film structure, the film morphology, and cell performances of these thin films and solar cells were discussed. The largest open-circuit voltage of 247.5 mV was obtained with Cu/Sn molar ratio of 1.67, therefore it is considered that the optimum value of Cu/Sn molar ratio of the evaporation materials in this fabrication method is vicinity of 1.67.

In addition, the effects to the characteristics of the Cu_2SnS_3 thin films and solar cells by the alkaline metals doping such as sodium and potassium were investigated. The film composition, the film structure, the film morphology, cell performances and quantum efficiencies of the Cu_2SnS_3 thin films and solar cells fabricated with alkaline metals doping were discussed. By sodium addition, the Cu_2SnS_3 thin films and solar cells were fabricated by sulfurization from the NaF/Cu/Sn stacked precursor deposited by the sequential evaporation of Sn, Cu and NaF. The cell performances of these Cu_2SnS_3 solar cells had an upward trend with increasing NaF/Cu molar ratio, and the Cu_2SnS_3 solar cell which was fabricated with NaF/Cu = 0.075 molar ratio demonstrated the record conversion efficiency of the Cu_2SnS_3 solar cells of 4.63%. By potassium addition, Cu_2SnS_3 solar cells fabricated by annealing KF/film-bilayer samples (film-bilayer means the thin film fabricated by sulfurization from the NaF/Cu/Sn stacked precursor) demonstrated the open-circuit voltage of 293 mV.

Finally, the effects of Ag doping on the characteristics of Cu_2SnS_3 thin films and solar cells were investigated. The $(Cu,Ag)_2SnS_3$ thin films and solar cells which were Ag doping of CTS were fabricated by sulfurization from the NaF/Sn/(Ag+Cu) stacked precursors deposited by sequential evaporation of Ag, Cu and Sn elements and NaF, and the Ag/(Ag+Cu) molar ratio of the evaporation materials and the sulfurization temperatures were varied. The film composition, the film structure, the film morphology, cell performances and quantum efficiencies of the $(Cu,Ag)_2SnS_3$ thin films and solar cells were discussed. The lattice spacing increased along Vegard's law with increasing the Ag/(Ag+Cu) molar ratio in films, and it is considered that the $(Cu,Ag)_2SnS_3$ was fabricated. The best solar cell fabricated with Ag/(Ag+Cu) = 0.05 at sulfurization temperature of 570 °C showed the conversion efficiency of 4.07%, and it was the first reports of $(Cu,Ag)_2SnS_3$ thin film solar cells. Furthermore, the expansion of the band-gap energy was seen with increasing the Ag/(Ag+Cu) molar ratio.