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Study of Growth of $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ Thin-Films by Spray-Printing Process and Their Application to Solar Cells

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Photovoltaic power generation, which is one of the renewable energy sources, is a promising solution for environment and energy problem because the method can generate electricity without CO_2 emission and from a huge energy source. For mass production of photovoltaic, I focus on $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe), which is a promising material since all the constituent elements are naturally abundant. The paper proposes a spray-printing as a new low-cost fabrication process for CZTSSe thin films, and their solar cell application is also reported. The method is an optimum approach to prepare thin films since the method has many advantages such as higher material utilization ratio and higher throughput with roll-to-roll processing than other non-vacuum methods, such as spin-coating.

First of all, I established a preparation method for CZTSSe thin film using spray-printing. The proposed fabrication process consists of three steps of nanoparticles synthesis, spray-printing, and sintering. Uniform nanoparticles were successfully synthesized by controlling the amount of solvent and temperature during raw material stirring. Uniform and dense thin films were achieved by adjusting the concentration of the ink and improving the dispersion method before spray-printing.

Next, to obtain guidelines for the preparation of high-quality CZTSSe thin films, I investigated the reaction route during sintering. Sintering of the CZTSSe thin films is carried out by introducing a precursor film together with Sn, S, and Se powder into a case, raising the temperature to 600 °C at a constant heating rate, and holding it. Even without sintering, the as-deposit film consisted of CZTSSe phase and the crystallinity was improved by raising the sintering temperature. This shows that there are no intermediate phases, such as binary and ternary compounds, during sintering, differing from other nonvacuum processes, indicating that the proposed method is a fabrication method for CZTSSe thin film with excellent composition control. From the observation of surface morphology and analysis of compositional and crystalline properties, it was revealed that the crystallization of CZTSSe progresses gradually in the S atmosphere at the time of heating, then selenization and expansion of grain occur at 550 °C or higher. It was also revealed that defects generate in the film due to the volume expansion of the CZTSSe crystal by selenization at 600 °C.

In order to solve the problem clarified by elucidation of the reaction route during sintering, I attempted relaxation of distortion due to the expansion of CZTSSe crystal by suppressing crystallization of the thin film before selenization using faster heating rate. From the evaluation of the surface morphology and crystallinity of the CZTSSe thin films sintered at various temperatures, the crystallization of the CZTSSe thin films before selenization was successfully restrained by increasing the heating rate from 10 to 100 °C/min, which lead the extension of the width of depletion layer due to the decrease in the carrier concentration in

the film and improvement of power conversion efficiency of CZTSSe solar cell, which consists of ZnO/CdS/CZTSSe/Mo structure, from 6.5 to 7.5 %. From computational consideration, it is presumed that the defect is a deep acceptor type defect.

Since the lattice constants of p-type CZTSSe and n-type CdS are different, electrons and holes recombine at CdS/CZTSSe interface, which leads to the deterioration of solar cell properties. To restrain the recombination of the carrier at the interface, post-annealing for improvement of crystallinity of CdS was investigated. The results of Raman measurement and device properties showed that the recombination at the CdS/CZTSSe interface decreased due to the improvement of crystallinity of CdS by applying post-annealing. Additionally, analysis of electrical characteristics in cross-section indicated that selenization and decrease in resistance near CZTSSe crystal grain boundaries occurred, and the collection region of minority carrier was expanded by post-annealing. This induces the decrease in series resistance, which resulted in the improvement of the fill factor of CZTSSe solar cells.

Finally, the simulation was conducted to obtain guidelines for further higher efficiency using solar cell capacitance simulator (SCAPS). CZTSSe solar cell fabricated from the proposed process, which shows the efficiency of 8.66 %, could be reproduced computationally with SCAPS. This simulation model showed that the primary problem of the CZTSSe solar cell fabricated by the proposed method is the recombination at the CdS/CZTSSe interface, CZTSSe bulk, and CZTSSe/Mo interface. In particular, the bulk defect concentration was about 100 times that of the Cu(In,Ga)Se₂ solar cell. The simulation revealed that the efficiency is greatly improved to 14.4 % by sulfurization of CZTSSe thin film surface, the introduction of Ge into the film near Mo, and reduction of point defect concentration by composition control of the film.