Fabrication of Chalcopyrite-type Compound Semiconductors by Electrodeposition for Solar Cell Application

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This thesis for a doctorate is to realize low-cost and high efficiency solar cells using chalcopyrite-type compound semiconductors such as $CuInSe_2$ (CIS) and $Cu(In,Ga)Se_2$ (CIGS) thin films by electrodeposition (ED). Merits of ED-technique are high material utilization and low power consumption in manufacturing. I have revealed and solved several issues of ED-chalcopyrite-type compound semiconductors to realize high quality films and high efficiency solar cells. As the issue, it is so difficult to deposit CIGS films consisted of four elements by single-step ED because the deposition potential varies according to the element. Especially, Ga-O compound is formed when the amount of Ga deposition is increased. This is the reason why the performances of solar cells with ED-CIGS films decrease. Next, $Cu_{2-x}Se$ which decreases the cell performance is formed due to excess Cu deposition in annealed ED-CIGS(or CIS) films. Therefore, $Cu_{2-x}Se$ was removed by KCN etching. However, pits and crevasses occurred and an adhesion between ED-CIGS(or CIS)/Mo interface was weakened due to the removal of $Cu_{2-x}Se$ formed in the grain boundary and between ED-CIGS/Mo interface. I have investigated "stacked ED films" to solve these issues. Firstly, I attempted to electrodeposit oxygen-free $CuGaSe_2$ (CGS) films to solve Ga-O compound in single-step ED, and fabricate CIGS films using CIS/CGS stacked films. A supporting electrolyte (pH buffer) was added in Cu-Ga-Se solution because the formation of Ga-O compound strongly depended on pH of the solution. As the result, oxygen-free CGS films were realized. In addition, smoother CGS films were improved with a smoothing agent and a brightener. I obtained the 2.9 % efficiency CIGS solar cell with the CIS/CGS stacked film as these improved results. Furthermore, high quality CIS films were realized by ED-In-Se/CIS stacked technique without KCN etching. These results indicate that CIGS films with the stacked ED-technique provide the foundation for the realization of very low-cost and higher solar cell and support the encouragements of broad use of solar cells.