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Study of Cu_2O Based Heterojunction Devices for Solar-to-Hydrogen Conversion

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Utilization of hydrogen as an energy source is attractive way to mitigate recent energy and environmental issues. Low-cost and mass production of hydrogen without emission of greenhouse gases is essential to realizing hydrogen society. Photoelectrochemical (PEC) water splitting is a key technology to produce hydrogen from sunlight. However, the solar-to-hydrogen conversion efficiency of current PEC cells is significantly low. In this thesis, development of highly efficient cuprous oxide (Cu_2O) based pn junction PEC cells was sought with only low-cost and scalable processes via the improvement of Cu_2O heterojunction solar cells.

First of all, comprehensive one-dimensional device simulation of Cu_2O based heterojunction solar cells was performed. The reliable simulation model which reproduced experimental reported solar cell characteristics was developed by taking into account defective layers between Cu_2O and n-type semiconductor. By using developed model, the strategies to improve the power conversion efficiency of Cu_2O heterojunction solar cells were clarified, that is, (i) high mobility and low defect density thin film Cu_2O photo absorbing layer, (ii) highly doped back surface layer, and (iii) n-type semiconductor layer with an electron affinity of around 3.2 eV deposited by low-temperature and low-damage.

For the Cu_2O absorber layer, effect of low-temperature post-deposition annealing (PDA) to electrochemically deposited Cu_2O (ECD-Cu_2O) thin films was intensively studied to enhance the optoelectronic properties. The free exciton luminescence was clearly observed in photoluminescence measurement at room temperature and the hole mobility was highly improved by PDA at around 150 °C independent of annealing atmosphere. The mobility of 18 $cm^2/V{\cdot}s$ was obtained by annealing at 150 °C for 60 min in N_2. This is the highest mobility obtained from undoped ECD-Cu_2O thin films on polycrystalline substrates. As the increase of the mobility, diffusion length of the ECD-Cu_2O thin films was also improved. On the other hand, the PDA at 200 °C deteriorated the optoelectronic properties because of the rapid increase of the mid-gap defects in ECD-Cu_2O thin films. These results provided a facile post-treatment for improving film properties and showed that the low-temperature process is especially important for Cu_2O based device fabrication.

Nitrogen doped Cu_2O (Cu_2O:N) thin films deposited with reactive magnetron sputtering were studied for an application to the back surface layer. Nitrogen doping effectively increased the hole concentration of Cu_2O thin films while decreased hole mobility. It was found that nitrogen incorporation was favored in O-poor deposition condition, suggesting that the N_O is a possible source of an acceptor. Theoretical calculation revealed that the decrease of the hole mobility with increasing hole density could be explained by ionized impurity scattering. The thickness dependence of the electrical and optical characteristics was also explored. The high hole concentration of above 1×10^{19} cm^{-3} and low mid-gap absorption of below 5% were successfully achieved by 20-nm-thick Cu_2O:N thin films. These results demonstrated that sputtered Cu_2O:N is a suitable material for the highly doped back surface layer.

For development of the suitable n-type semiconductor layer for Cu_2O based devices with a scalable process, low-temperature metalorganic chemical vapor deposition (MOCVD) using trimethyl gallium (TMGa) and water was investigated. It was found that nano-crystalline or amorphous thin films were obtained at a deposition temperature below 182 °C, while crystallized nanowires formed at a temperature above 227 °C. Detailed structural and chemical analysis revealed that the obtained materials were mixture of gallium hydroxide, gallium tohdite, and gallium oxyhydroxide containing small amount of carbon contamination. This impurity carbon was originated from monomethyl gallium which was produced by imperfect oxidation of TMGa. The PDA to these films in ambient air was also conducted to investigate the effect on structural and chemical properties. It was showed that the 300 °C PDA effectively reduced remained carbon through the oxidation of monomethyl gallium.

Finally, the developed techniques and materials were applied to Cu_2O solar cells. The significant improvement by the PDA to ECD-Cu_2O thin films was not confirmed because of the device fabrication process. However, the PDA at above 200 °C deteriorated the solar cell performance especially short-circuit current density due to the reduction of the minority carrier diffusion length. This result showed the importance of the device fabrication temperature for the ECD-Cu_2O based devices. The insertion of the Cu_2O:N thin films did not affect the device performance because of the low optoelectronic properties of the ECD-Cu_2O absorber, while it was suggested that the alternative metal electrodes instead of expensive gold or platinum can be used for the ECD-Cu_2O devices. The photovoltage gain was observed by using the 5-nm-thick MOCVD deposited gallium oxide related film with subsequent 300 °C annealing. However, a drastic improvement of the device performance was not achieved. Further investigation of the carrier collection properties of ECD-Cu_2O solar cells by external quantum efficiency (EQE) and electron beam-induced current measurements revealed that the present device had high EQE of around 0.5 at a wavelength of 550 nm thanks to the precise temperature control while carrier collection was prevented by the grain boundary recombination.