Solution Processing of $Cu(In_xGa_{1-x})(S,Se)_2$ Absorber Layer for Thin Film Solar Cells

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Submitted by

Maurya Sandeep Pradeepkumar

DEPARTMENT OF CERAMIC ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY
(BANARAS HINDU UNIVERSITY)
VARANASI – 221005
INDIA

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Chapter VIII

Conclusions and Scope of Future Research

In this chapter, a summary of the finding of this thesis is given. The major conclusion drawn from the work are enumerated and the scope of future work in this area has been suggested indicating possible refinement and modifications.

VIII.2 Brief Summary and Conclusions

The thesis discussed the synthesis of wurtzite(wz) $CuIn_xGa_{1-x}S_2$ (X=0-1) nanoparticles (NPs), their deposition as thin films and selenization to obtain a chalcopyrite phase with enlarged grain sizes and their application as solar cell absorber. This work has demonstrated an alternative fabrication approach utilizing wz-CIS nanoparticle ink which was deposited using high-throughput spray deposition technique to achieve large grained ch-CIS photovoltaic absorber layer.

In Chapter I, a general introduction about importance of solar energy as an alternative source to fulfil the energy demand is given. It gives a brief idea about the solar cell materials and their present market share, and the need for developing a high throughput processing route. This chapter also gives the motivation behind the thesis work.

Chapter II presents a brief description of the history and current status of CIGS solar cell absorber layers, the phase relations in Cu_2S-In_2S_3 and Cu_2Se-In_2Se_3 systems, and a survey of different vacuum and solution-based fabrication techniques. The main focus is on ink preparation for high-throughput and low-cost spray deposition technique.

Chapter III deals with the hot-injection synthetic method using Schlenk line set-up to synthesize the wz-$CuIn_xGa_{1-x}S_2$ NPs, and described the ink-formulation. Further, characterization techniques used to investigate the structure and properties of the synthesized nanoparticles and films are discussed in this chapter.

Chapter IV establishes the formation and growth mechanism of wz-$CuInS_2$(CIS) NPs using the hot-injection method with amine-thiol ligand, where it has been confirmed that the CIS NPs forms by incorporation of indium into the Cu_2S crystal nuclei through the diffusion and/or cation exchange. The most significant conclusions obtained from this study are the following:

1. Formation and growth of Cu_2S take place at the earlier stages which later converts into CIS formed with the diffusion of In^{3+} ion. A systematic ex-situ study of the growth of oval shape wz-CIS NPs reveals that growth rate is faster in lateral direction than in the width direction.
2. HRTEM and FFT patterns indicates to the preferential growth of NPs along the [0002] direction while the side facets are enclosed by $(10\bar{1}1)$ and $(10\bar{1}0)$ crystallographic planes.
3. Elemental mapping of a cluster of NPs shows homogeneous distribution of all the elements Cu, In, and S.

Therefore, it is observed that by carefully changing the temperature and control over active ligand, it is possible to control the growth of NPs.

Chapter V is concerned about synthesis of wz-$CuIn_xGa_{1-x}S_2$ with x varying from 0 to 1 and its effect on morphology and phase formation. The following conclusions could be drawn:

1. This study shows phase separation on substitution of gallium in place of indium ion in wz-$CuIn_xGa_{1-x}S_2$(x=0-1).
2. Phase pure wz-$CuInS_2$ (x=1) and wz-$CuGaS_2$(x=0) are single-phase wurtzite structures with oval and predominantly hexagonal morphology, respectively.
3. Two phases are identified for x=0.7. $CuIn_{0.7}Ga_{0.3}S_2$ has rod-like (In-rich) and irregular hexagonal (In–Ga) morphologies. As gallium substitution increases to x=0.5 ($CuIn_{0.5}Ga_{0.5}S_2$), a third phase relatively rich in Ga (having tadpole morphology) appears which is more prominent at higher Ga substitution ($CuIn_{0.3}Ga_{0.7}S_2$) while the In-rich phase diminishes.
4. Substitution of gallium also lowers the lattice parameter *a* and *b*, resulting in a reduction in particle size. The bandgap increases with the gallium substitution.

In Chapter VI, we have investigated the phase transformation and grain growth of spray deposited wz-CIS absorber layer during selenization. Followings are the most significant conclusions drawn:

1. Wurtzite to chalcopyrite phase transformation and grain growth are two distinct phenomena and are not coupled in the case of CIS.
2. A complete phase transformation (wurtzite to chalcopyrite) takes place by heating up to 400 °C for 15 min with relatively lower Se substitution ($Se/(Se+S)\approx0.5$), while the grain growth is temperature-dependent and requires greater Se diffusion ($Se/(Se+S)>0.7$).
3. DSC thermogram shows signature of second-order character with a possible zincblende-CISSe intermediate phase on phase transformation.

In Chapter VII, the optimization of processing parameters for CIS absorber layer through spray deposition and their implication on the device fabrication has been studied. The major conclusions drawn are as follows:

1. Spray deposited film uniformity, crack, void and surface roughness can be controlled through variations in substrate temperature, spray rate and concentration of ink.
2. A pinhole and crack free absorber layer is obtained at substrate temperature 250 ^oC, using a spray rate of 2 ml/min, while the concentration of ink is 2.8 mg/ml (2.8 mg of CIS NPs in 1 ml of a solvent mixture,1-DDT: Toluene:: 1:10).
3. Selenization of wz-CIS film results in the formation of phase pure ch-CISSe phase with micron size grain.
4. Solar cell efficiencies are about 2.12 and 7.35% for wurtzite and chalcopyrite CIS based devices, respectively.

VIII.2 Suggestions for Future Work

We believe the work presented in the thesis will provide an understanding of the mechanism of wz-$CuIn_xGa_{1-x}S_2$ NPs formation with control over morphology and phase purity, and the effect of process parameters on the formation of absorber layer through spray coating. Although the main objectives are largely met, there are few suggestions, which are beyond the scope of the present work. The following issues may be looked at in future:

1. At present, the formation mechanism and growth of wz-CIGS NPs is understood, however as to why the growth of NPs in lateral direction is

more compared to width direction still remains unclear. Understanding this phenomenon will provide a way to modify shape of NPs with a variation of ligands. And that could help to obtain elongated rod-like morphology, which allows easy flow of charge carriers.

2. Wurtzite to chalcopyrite phase transformation has been observed to happen during selenization at the 400 °C; however, the exact mechanism of grain growth is still unclear. It is clear that a higher selenization temperature results in a thicker large-grained layer and a thinner fine-grained layer. In case of CZTS, grain growth is initially fast and then slows down for longer selenization times. However, in case of CIGS this needs to be confirmed.
3. Radiative annealing (rapid annealing) can be adopted for selenization as an alternative approach which will significantly reduce the time as well as cost.
4. Bandgap grading has been a tested approach to improve the performance of CIGS solar cells, where a proper distribution of a Ga/In and Ga/Cu is graded through the absorber layer thickness. It is very well established for vacuum-based method; however, only a few reports discuss bandgap grading in solution processed of the CIGS absorber layers. Bandgap grading profile can be incorporated during spray deposition by synthesising wz-CIGS NPs ink with varying composition and sequential deposition or using multiple spray nozzles.