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

Thesis submitted in partial fulfillment for the Award of Degree

Doctor of Philosophy

Submitted by

Maurya Sandeep Pradeepkumar

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

Roll No. 16031005

JULY 2022

CERTIFICATE

It is certified that the work contained in the thesis titled **"Solution Processing of $Cu(In_xGa_{1-x})(S,Se)_2$ Absorber Layer for Thin Film Solar Cells"** by **"Maurya Sandeep Pradeepkumar"** has been carried out under our joint supervision and that this work has not been submitted elsewhere for a degree.

It is further certified that the student has fulfilled all the requirements of Comprehensive Examination, Candidacy and SOTA for the award of Ph.D. degree.

Supervisor

Dr. Mohammad Imteyaz Ahmad
Assistant Professor
Department of Ceramic Engineering
IIT(BHU), Varanasi

Co-Supervisor

Dr. Joysurya Basu
Associate Professor
Department of Metallurgical Engineering
IIT(BHU), Varanasi

DECLARATION BY THE CANDIDATE

I, **Maurya Sandeep Pradeepkumar**, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the joint supervision of **Dr. Mohammad Imteyaz Ahmad** and **Dr. Joysurya Basu** for a period from **July 2016** to **July 2022** at the "**Department of Ceramic Engineering**", Indian Institute of Technology (BHU), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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Place : Varanasi (MAURYA SANDEEP PRADEEPKUMAR)

CERTIFICATE BY THE SUPERVISORS

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(Supervisor)
Dr. Mohammad Imteyaz Ahmad
Assistant Professor
Department of Ceramic Engineering
IIT(BHU), Varanasi

(Co-Supervisor)
Dr. Joysurya Basu
Associate Professor
Department of Metallurgical Engineering
IIT(BHU), Varanasi

Head of Department Ceramic Engineering

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Candidate's name : Maurya Sandeep Pradeepkumar

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Date: July 15, 2022

Place: Varanasi (Maurya Sandeep Pradeepkumar)

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(MAURYA SANDEEP PRADEEPKUMAR)

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PREFACE

Solar photovoltaics (PVs) is one of the renewable energy conversion technologies that is gaining importance globally for its low maintenance and longer operating life. The free and profusely abundant solar energy can be collected by PV devices and may directly be converted into electricity. At present, silicon-based PVs account for over 90% of worldwide module production. However, due to their rigidity, costlier fabrication, and inefficient light absorption, thin film solar cells are being explored. Thin film solar cells have low manufacturing cost, less material usage, high absorption coefficient and are scalable. Thin film solar cells have the potential to convert sunlight into electricity at a lower overall cost. Currently, commercially available most efficient (~19%) thin film solar cells are based on polycrystalline $Cu(In_xGa_{1-x})(S,Se)_2$ (CIGS) absorber layers. CIGS has a direct and tunable bandgap (1.5–2.0 eV), a high absorption coefficient ($\sim 10^5$ cm^{-1}), coupled with greater radiation resistance as compared to crystalline silicon solar cells. For fabricating state-of-the-art high efficiency devices, the CIGS layer is deposited by co-evaporation using an elemental source under high vacuum conditions. Vacuum-based processing technologies have high operating costs and are not easily scalable. Solution-based processing techniques have constantly received attention due to low cost, scalability, control on composition and growth. However, the performance of solution-processed CIGS (18.7%, lab scale) absorber-based devices is much lower than the vacuum processed ones (23.35%, lab scale). Several factors that hamper the device performance of solution processed films include elemental impurities, unburnt impurities from solvents and precursors (C, N, O, Cl etc.), the presence of voids and surface roughness, fine-grained layer with high boundary density. We

have tried to mitigate some of the stated issues and demonstrated the processing of solar cell grade high density, large grained absorber layer through spray deposition.

Typically, chalcopyrite(ch), zinc-blende and wurtzite (wz) are the three polymorphs of CIS, with chalcopyrite being the thermodynamically stable form at room temperature (RT). Recently, it has been demonstrated for $Cu_2ZnSn(S,Se)_4$ (CZTS) that phase transformation can assist a rapid grain growth. It was shown that wz-CZTS nanoparticles, when heated to about 500 °C in the presence of Se vapour, transform to kesterite phase accompanied by rapid grain growth where grains were shown to grow upto a micrometer in size. Similar to CZTS, the wurtzite phase in CIGS is also a high-temperature phase (stable between 1045-1090 °C) and is metastable at room temperature. The wurtzite phase of CIGS has been reported to stabilize in the nano-regime. Many researchers have recently reported the synthesis of wz-CIGS nanoparticles through wet chemical route.

The first step was to synthesize a phase pure wz-CIS nanoparticle. The metastable wz-$CuInS_2$ (CIS) nanoparticles were synthesized by a solution-based processing technique. The mechanism of wz-CIS NPs formation during solution processing was studied. The formation of CIS was found to depend on various factors such as temperature, relative reactivity of copper and indium in solution, type of ligand, etc. It was observed from XRD and TEM, Cu_2S nucleated and grew at the earlier stages and later In_2S_3 formed. On increasing temperature above 200 °C, CIS formed with the diffusion of In^{3+} ion. Wurtzite CIS nanoparticles preferentially grew along one direction while the width nearly remained constant. The HRTEM images and the FFT patterns indicated that the oval shaped wz-CIS NPs grew along the [0002] direction and it was enclosed by $(10\bar{1}1)$ and $(10\bar{1}0)$ crystallographic facets. FTIR

spectra recorded at different stages of synthesis (50–310 °C) pointed towards the ligand exchange mechanism after the addition of sulfur source at 160 °C. The synthesis of wurtzite CIS NPs through the wet-chemical route using amine-thiol ligand confirmed that the CIS NPs formed by incorporation of indium into the Cu_2S crystal nuclei through the diffusion and/or cation exchange.

Once the CIS was synthesized, Ga was substituted for In, and its influence on the structure and morphology of particles was studied. Nanocrystalline $CuIn_xGa_{1-x}S_2$ (x = 1, 0.7, 0.5, 0.3, 0) wurtzite particles were synthesized by solution process. It was observed that gallium incorporation in $CuInS_2$ results in structural distortion, non-homogeneous shape, and size distribution of particles. As-synthesized $CuInS_2$ (CIS) and $CuGaS_2$ (CGS) nanoparticles were single-phase wurtzite structures, whereas $CuIn_{0.7}Ga_{0.3}S_2$, $CuIn_{0.5}Ga_{0.5}S_2$, and $CuIn_{0.3}Ga_{0.7}S_2$ had three wurtzite phases having In-rich, In–Ga, and Ga-rich compositions. The shape of the resulting nanoparticles were either elongated, polygonal, or tadpole, depending on the phase composition. In-rich particles had elongated rod-like morphology, the In–Ga particles were irregular hexagonal, while the Ga-rich phase formed with a tadpole morphology. It has been observed that the morphological evolution strongly depends on the nature of the composition separation of In and Ga.

The wz-CIS nanoparticles were dispersed and was uniformly deposited over the Mo/SLG substrate by spray deposition using nitrogen as carrier gas. The wz-CIS film (grain size ≈25nm) was selenized to obtain large-grain chalcopyrite CISSe film (grain size ≈700nm). Wurtzite (CIS) to chalcopyrite (CISSe) phase transformation and grain growth at various selenization temperatures of 350, 400, 450, 500 and 550 °C was studied. XRD and high-resolution scanning electron microscopy

(FESEM) indicated that the grain growth depended on the Se diffusion. By 400 °C, the complete film transformed from wurtzite to chalcopyrite phase; however, the grain growth required greater selenium and temperature. Differential scanning calorimetry (DSC) revealed that the phase transformation temperature was sensitive to the heating rate and had a strong second-order character.

Further, the device was fabricated using the as-deposited wurtzite CIS and selenized chalcopyrite CISSe as absorber films with common device architecture SLG/Mo/(wz-CIS or ch-CISSe)/CdS/i-ZnO/Al-ZnO/Au. The homogenous and compact layer of CdS (~100nm) was deposited in a chemical bath maintained at pH10, which was subsequently dried at 120 ^{o}C by radiative annealing. The compact and transparent conductive oxide film, i-ZnO (~60nm) and Al-ZnO (~300nm) were deposited by the RF sputtering, which had a bandgap of 3.3 and 3.45 eV, respectively. Finally, Au front contact was deposited using thermal evaporation. The fabricated device with as-deposited wz-CIS and selenized ch-CISSe absorber layers had PCEs 2.12 and 7.35%, respectively.

The thesis shows the alternative approach for CIS device fabrication, where spray deposition technique utilizing wz-CIS nanoparticle ink is a promising, low-cost and scalable process for the deposition of CIS absorber layers. The layer shows phase transformation and grain growth (micron size) on selenization. The process can be further improved by incorporating multiple ink compositions to regulate Ga/Ga+In gradient to improve the efficiency. Further developments should germinate industrial interest in non-vacuum deposition processes for low-cost solar cell production.