

Study on doctor blade and spin coated cuingase2 thin films

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ABSTRACT

This report deals synthesis of CuInGa (CIG) nano materials along with doctor blade and spin coated thin films selenization and their physical properties. The doctor blade and spin coated CIGS/SLG thin films thicknesses are obtained 2 μm and 2.95 μm . Raman spectroscopy of these thin films leads the chalcopyrite phase formation by exhibiting the peak at wave number 171 cm^{-1} . The well-developed grain growths of spin coated thin film are appeared in the surface morphology. While the grain growths developments in doctoral blade coated thin film is rather hard and fuzzy. EDS measurement recognised the existence of the compositional ratio presence of the alloying elements Cu, In, Ga and Se. The doctor blade and spin coated CIGS/SLG thin films are exhibited the UV- Visible transmission peak in the wave length range 240 nm 320 nm. The optical energy band gaps for the doctor blade and spin coated CIGS thin films are obtained 1.41eV and 1.5 eV.

keywords: CIGS; Thin films; Raman spectra; UV-Visible.

1. Introduction

Energy consumption rising in human daily life and more demands in future. To fulfilling future energy demands investigators have recognized the promising renewable energy resources one of the potential technology which can deliver. Based on the fact sun in our solar system provides us an abundant source of sustainable energy. The abundantly provides sun energy is enough for common humanity use. The enough amount of sunlight can be use for the common electricity by conversing photovoltaic (PV) devices^[1].

The multilayered PV like CuInGaS₂ (CIGS), Cu(In,Ga)Se₂ (CIGSe) are identified as an potential area for the research, due to their enhanced efficiency, with long-time stability and excellent durability^[2-4]. Specifically active layer CIGS material has been recognized as exceptionally well due their high absorption coefficient (around 10⁵ cm^{-1}) with strong sunlight absorption ability. As applicability point of view CIGS active layer material thin films are desired. The typical thickness of this layer is well defined in the range 1.5 μm to 3 μm for the best performing devices. The various advantages CIGS active layer material make them an excellent candidate as an absorber layer for large scale production of thin film PV modules^[5].

Usually high yield CIGS devices efficiencies are reported with the vacuum processes like co-evaporation and sputtering ^[4].With the several advantages vacuum process technologies also have serious issues for the large scale manufacturing, due to their low productivity, high production costs and compositional uniformity^[5]. To overcome these shortcomings investigators have paid attention toward alternative non-vacuum processes. The non-vacuum processes can have significant advantages like lower fabrication costs, higher productivity, uniformity and well stoichiometrical ratio. Yet, it is reality the alternative non-vacuum processes based CIGS devices could not achieve same efficiencies as high-vacuum processes. But alternative non-vacuum processes stand out as competitive production routes in the future^[6]. The CIGS non-vacuum approaches predominately have been investigated from the techniques like electrodeposition, spray pyrolysis, printing etc^[7- 9].

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In spite of different strategies exist for reducing carbon contamination in solution-processed CIGS films. The highest device efficiency for the solution-processed CIGS PV has been achieved with the selenized hydrazine-derived molecular reactants^[10]. With this process major drawback its high toxicity, potential explosive and cost of hydrazine for the manufacturing process^[10]. To resolve these issues investigators have presented several technical reports on CIG nano ink synthesis and their thin films on different substrates from different techniques^[11]. Spin coating and doctor blade coating are also identified cheaper deposition techniques for the large scale.

Goal of this report to present non-toxic nitrate route CIG nano ink and pest synthesis for the thin films deposition from spin coating and doctor blade coating techniques. The five times spin and doctor blade coated selenized thin films thickness profile, chalcopyrite phase formation Raman verification, Scanning Electron Microscopic (FESEM) grain growths formation with compositional Energy Dispersive Spectrum (EDS) analysis, UV-Visible transmission profile and optical energy band gaps are studied.

2. Experimental Details:

Precursor solution of the CIG was prepared by dissolving the appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (99.999%), $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.99%), and $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ (99.999%) in ethanol (80 mL) with terpineol (20 ml). The solution was then stirred vigorously for 3 h, under maintained temperature around 50°C , a viscous blue colour CuInGa (CIG) solution with rheological properties was obtained for the spin coating. Afterward half part of the originally prepared solution was separated. The separated solution again heated at 150°C under the continuous stirring a viscous dark green colour CIG pest was achieved for the doctor blade coating.

The CIG solution spin coating was performed on 2.5 cm x 2.5 cm soda lime glass (SLG) substrate at 3000 rpm. Subsequently the spin coating deposited thin film was dried on hot plate at 150°C . This process was done for all five times. While, CIG viscous dark green colour pest was deposited on the 2.5 cm x 7 cm SLG substrate from the doctor blade coater. During the spin and doctor blade coating of CIG the attention was on homogeneity of thin films thickness. The spin coated and doctor blade coated well dried thin films were used for the selenization. Samples selenization process were done at $350^\circ\text{C} \pm 20^\circ\text{C}$ under the continuous flow of N_2 in Se vapour environment. It was ensured the CIGS thin films composition ratio 1:0.7:0.3:2. The schematic including prepared CIG nano material for spin and doctor blade coating, coating process, selenization step and photographs of the selenized thin films is given in

Figure 1.

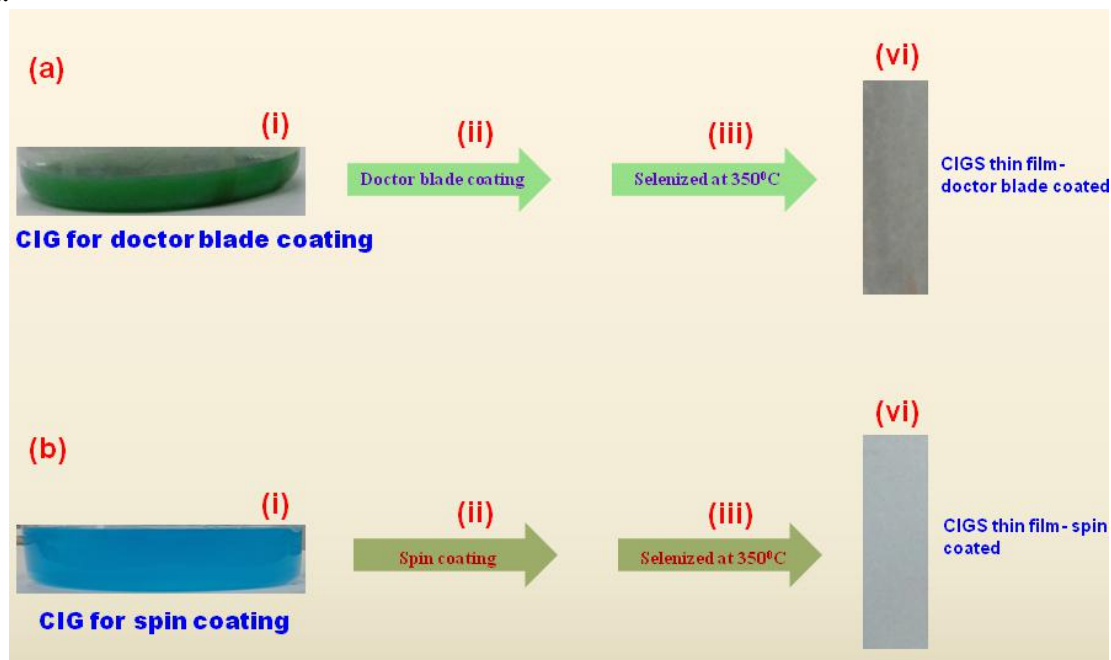


Figure 1: Schematic, (a-i) CIG pest for the doctor blade coating, (ii) CIG/SLG thin film deposition step, (iii) step of selenization, (iv) doctor blade coated CIGS thin film photograph.

Schematic, (b-i) CIG nano ink for the spin coating, (ii) CIG/SLG thin film deposition step, (iii) step of selenization, (iv) spin coated CIGS thin film photograph.

Thicknesses of the both methods made CIGS/SLG thin films were determined from the thickness profillometer. To confirm the chalcopyrite phase in these thin films the Raman spectroscopic measurement were performed. The surface structural morphologies of the thin films were examined from the Scanning Electron Microscope (FESEM). To confirm the prepared CIGS material nano formation and evaluate the optical energy band gaps for the UV- Visible transmission spectra were recorded from the spectrometer.

3. Results and Discussion:

The five times spin coated and analogues doctor blade coater adjusted distance scale between the knife and substrate process, CIG /SLG thin films are obtained. After selenization (CIGS /SLG) thin films appropriate thickness knowledge is an important parameter for the optimization of spin and doctor blade coated active layer. The thickness measurement of the spin and doctor blade coated CIGS /SLG thin films is performed from the thickness profillometer. The obtained thickness profillometer result plots for these different processes coated CIGS/SLG thin films is given in Figure2.

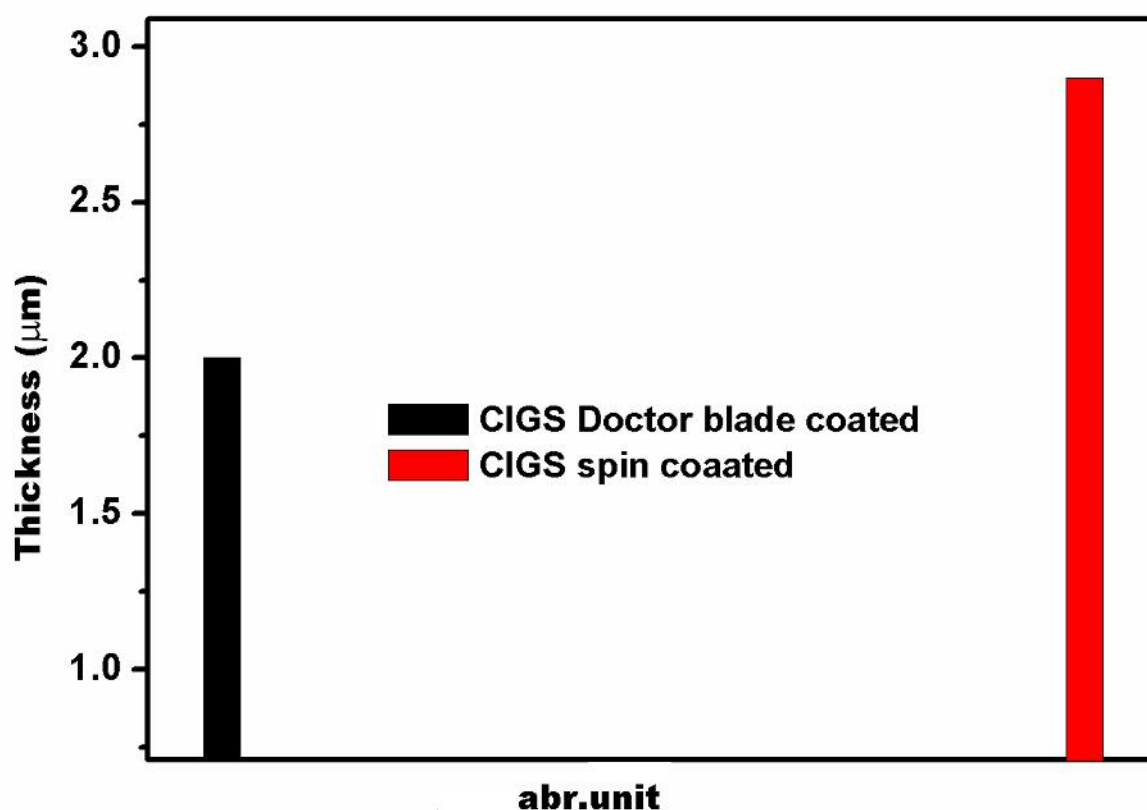


Figure 2: Thickness profile plots for the doctor blade and spin coated CIGS/SLG thin films.

From the plot it is clear doctoral blade coated selenized film thickness (2 μm) lesser than the spin coated CIGS film (2.95 μm). This result also gives thicknesses of these different processes deposited CIGS/SLG thin films are falling in well recognized range (1.5 μm to 3 μm) for the CIGS active layer martial^[12].

For the verification of the chalcopyrite phase formation in these two different processes deposited CIGS/SLG thin films we were performed the Raman spectroscopic measurement, in the wave number range upto 600 cm⁻¹. The obtained Raman spectrum for these CIGS/SLG thin films is exhibited in Figure3.

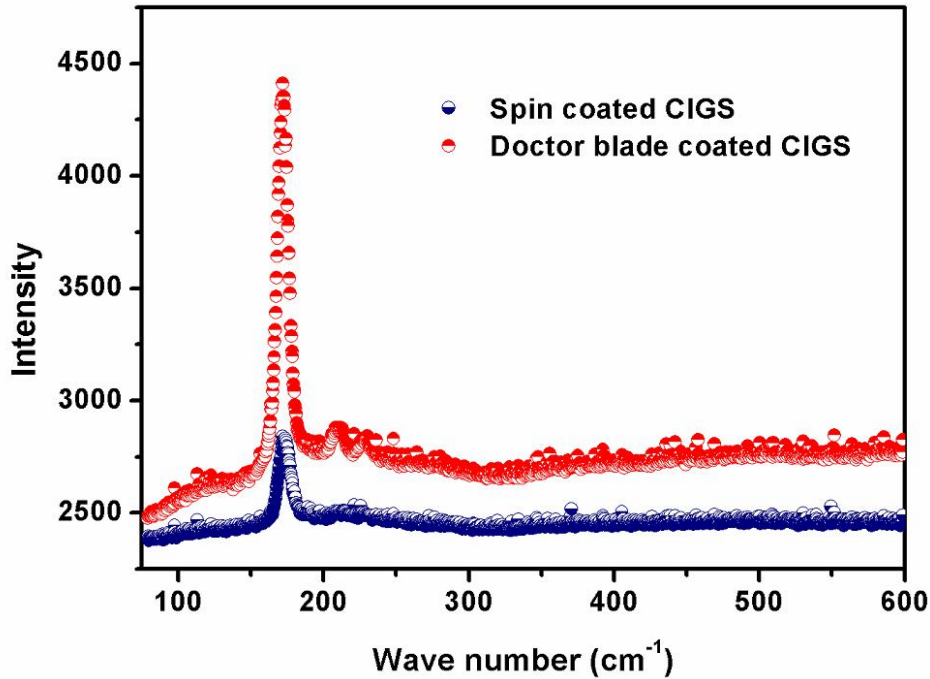


Figure 3: Raman spectrum for the doctor blade and spin coated CIGS/SLG thin films.

Raman peak of PV active chalcopyrite phase CIGS material appears at 171 cm^{-1} for spin and doctor blade coated thin films^[13,14]. The higher value of the Raman peak intensity for the doctor blade coated CIGS/SLG thin film might be due to its high order surface reflectivity in comparison to spin coated thin film. The non appearance of other prominent Raman peaks in spin and doctor blade coated CIGS/SLG thin films reveals a homogeneous chalcopyrite phase formation. The homogeneous chalcopyrite phase formation makes them potential CIGS/SLG thin films for the PV application^[13,14].

To verify the microstructural surface grain growths in these thin films performed the FESEM measurement. Surface morphology and EDS patters for the spin coated CIGS/SLG thin film is exhibited in **Figure 4** (a, b).

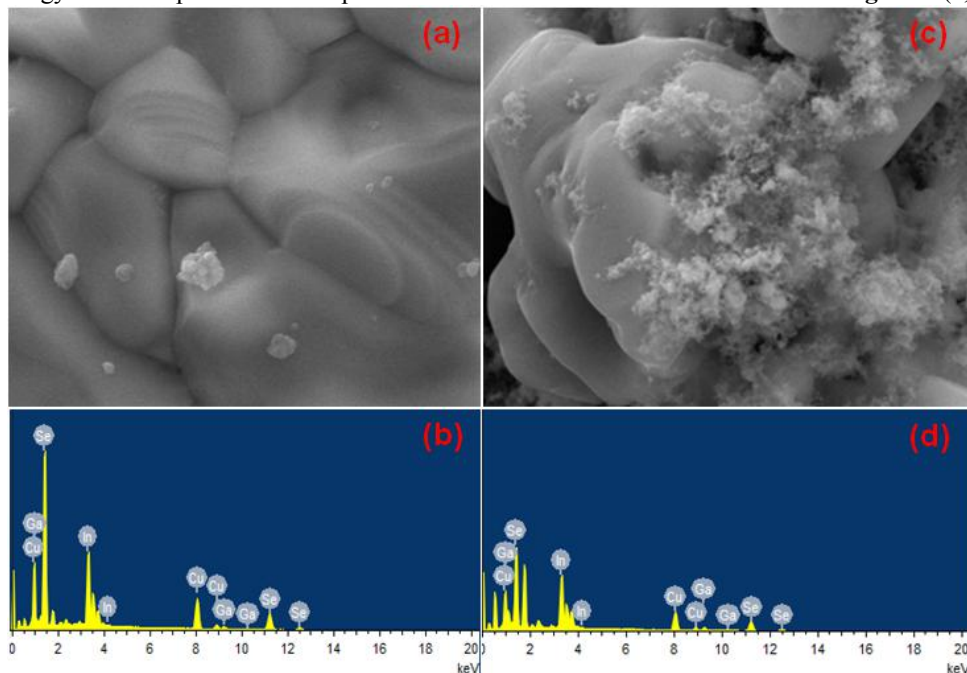


Figure 4: FESEM surface morphology and EDS spectrum; (a, b) for the spin coated CIGS/SLG thin film; (c, d) for the doctor blade coated CIGS/SLG thin film.

While the surface morphology and EDS patters for the doctor blade coated CIGS/SLG thin film is given in Figure. 4 (c, d). The surface morphological analysis of spin deposited CIGS/SLG thin film gives well developed grains growths with a compact grain connectivity (See Figure.4 (a)), while a fewer grain growths (rigid hard and fuzzy) and gains connectivity is appeared for the doctor blade coated CIGS/SLG thin film (See Figure.4 (c)). This may be due to involvement of two distinct deposition techniques. However, both processes deposited thin films EDS patters gives the presence of alloying elements Cu, In, Ga and Se in their compositional ratio.

It is well established fact that nano dimension materials should exhibit UV-Visible absorption or transmission peak upto 500 nm range^[15,16]. Therefore, we have performed the UV-Visible transmission measurement for these spin and doctor coated CIGS/SLG thin films. The obtained UV-Visible transmission spectrums of these two different processes deposited CIGS/SLG thin films is exhibited in **Figure 5** (a, b).

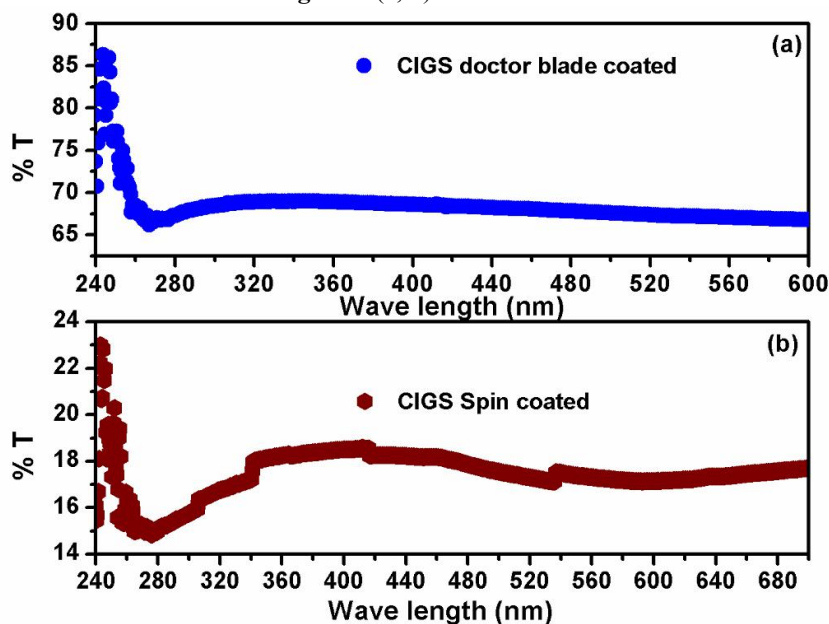


Figure 5, (a, b); UV-Visible transmission spectra for the doctor blade and spin coated CIGS/SLG thin films.

Both processes deposited CIGS/SLG thin films have shown the UV-Visible transmission peak below the 280 nm. This confirms the nano dimension formation of CIGS active layer material. Additionally, with the help of UV-Visible transmission spectra can also obtain optical energy band. Knowledge of the optical energy band gap is an important parameter for the PV active layer material. To evaluated the direct optical energy band gaps for two different processes deposited CIGS/SLG thin films Tauck plots is given in **Figure 6** (a, b).

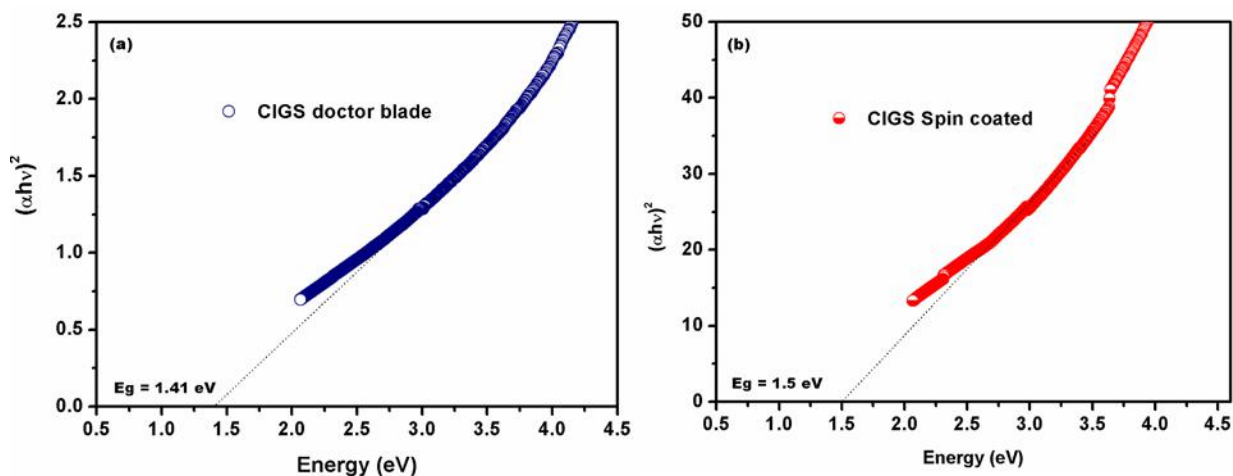


Figure 6, (a, b); Tauck plots to obtain optical energy band for the doctor blade and spin coated CIGS/SLG thin films.

Optical energy band gaps for these thin films can be obtained by extrapolation of normal line through the spectrum curve age. The x-axis cut point of the extrapolated normal line directly gives the value of the optical energy band gap for these thin films. The evaluated optical band gap (1.41 eV) of doctor blade coated thin film is fewer than spin coated thin film (1.5 eV). This result demonstrates spin coated CIGS/SLG thin film optical energy band gap is more appropriate for the PV use than doctor blade CIGS/SLG thin film.

4. Conclusions

In conclusive remarks, we have synthesized CIG material with the non toxic route and deposited their thin films on SLG substrates by the doctor blade and spin coating methods. To make CIGS chalcopyrite phase composition the deposited CIG thin films have selenized. The doctor blade and spin coated CIGS/SLG thin films thicknesses have demonstrated, it falls in the typical applicable range for the PV active layer material. Raman spectroscopic result has revealed the chalcogenide phase formation in doctor blade and spin coated CIGS/SLG thin films. The FESEM surface morphological outcome has verified the well developed grain growths with superior grains connectivity for the spin coated CIGS/SLG thin film as compare to doctor blade coated thin film. Stoichiometry of the CIGS composition for the spin and doctor blade thin films have been verified from the EDS patterns. With the help of UV-Visible transmission patters of the doctor blade and spin coated thin films the nano dimension formation in CIGS active layer has confirmed. The optical energy band gaps for the doctor blade and spin coated CIGS/SLG thin films have obtained 1.41 eV and 1.5 eV. On the basis of the outlined technical physical properties the spin coated CIGS/SLG thin film can have more utility than doctor blade coated thin film.

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